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Stabilization of Highly Reactive Group 13 and 15 Species

Author
Ruiz, David Anthony

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Stabilization of Highly Reactive Group 13 and 15 Species

A dissertation submitted in partial satisfaction of the requirements for the degree of
Doctor of Philosophy

in

Chemistry

by

David Anthony Ruiz

Committee in charge:

Professor Guy Bertrand, Chair
Professor Adah Almutairi
Professor Joshua Figueroa
Professor Clifford Kubiak
Professor Emmanuel Theodorakis

2015

The Dissertation of David Anthony Ruiz is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

Chair

University of California, San Diego
2015

DEDICATION

This is dedicated to my parents

For their endless love, support, and encouragement

For all the sacrifices and struggles they went through to give me this opportunity

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LIST OF ABBREVIATIONS

Ad: 1-adamantyl

Ar: Aryl

DFT: Density functional theory

Dipp: 2,6-diisopropylphenyl

Dme: 1,2-dimethoxyethane

EPR: Electron paramagnetic resonance

HOMO: Highest occupied molecular orbital

***i*Pr**: Isopropyl

KHMDS: Potassium bis(trimethylsilyl)amide

LUMO: Lowest unoccupied molecular orbital

Me: Methyl

Mes: Mesityl, 2,4,6-trimethylphenyl

NBO: Natural bond order

NHC: N-heterocyclic carbene

NMR: Nuclear Magnetic Resonance

Ph: Phenyl

SOMO: Singly occupied molecular orbital

***t*Bu**: Tertbutyl

Tf: Trifluoromethanesulfonyl

THF: Tetrahydrofurane

Tht: Tetrahydrothiophene

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ACKNOWLEDGEMENTS

I would like to first thank Prof. Adah Almutairi, Prof. Joshua Figueroa, Prof. Clifford Kubiak and Prof. Emmanuel Theodorakis for taking time to evaluate this work.

To my advisor, Prof. Guy Bertrand, thank you so much for giving me the opportunity to be a part of this lab. I have definitely grown a lot over the course of the past years, and have been greatly molded by what we in lab call “Guy style.” I truly appreciate the times when I would prepare a draft and you go would through it word by word with me, sometimes for several hours, making huge improvements and allowing me to see how to make the most of every detail and tell the best story. It has been a privilege to have an advisor who gave me the freedom to pursue what I was interested in, and also gave advice and discussed the results, no matter how crazy they became. I am forever thankful for the time spent absorbing as much knowledge from you and the trust and time you put in me. Thank you Guy.

I am also grateful to Prof. Gernot Frenking. The short time I spent in Marburg where I learned about computational chemistry was my first research experience outside of the U.S. It was a great learning experience, and I also have to thank Paul Jerabek for taking time to train me.

X-ray crystallography became an integral part of my studies and I give many thanks to Prof. Arnold Rheingold and Dr. Curtis Moore for taking time to train me and help me with the structures I could not solve. I appreciate all the help from Anthony Mrse when it came to NMR spectroscopy.

When I first started in the lab, Mo took a lot of care to make sure I learned the techniques needed to handle the reactive compounds of the lab. He was extremely helpful and I am very thankful for the all the support throughout the years. No matter how lost I was with the chemistry, Mo was patient and pointed me towards how to best proceed. Thanks for all the advice that helped make me become the chemist I am today.

Michele also played a big role during my time in the lab. We always shared the same lab room, and I saw how much work you put into keeping the lab functional and running. I learned how to contact companies and get discounts for items and helped with some of the orders. With your trust, I learned things that will be vital if I ever set up my own lab and need to consider a budget. Aside from that, it was always a pleasure discussing weekend plans, current events, chemistry progress, future ideas, dogs…. Thank you for your kindness and words of encouragement throughout the years.

David M. was the third member of the CNRS when I first joined the lab. We had many great times over dinner, especially with raclette (melted cheese). You were always helpful to me and I am very grateful to have spent most of my time with you around. Best wishes on your independent career.

I was heading towards finishing my stint in the lab when the last CNRS member, Rodolphe Jazzar, joined the lab. I had great times discussing chemistry with you and am forever grateful for your help with solving those tricky crystal structures. Best wishes on your future with the lab.

I have seen many, many amazing chemists throughout my time in the lab. From each, I learned something unique and have adapted it throughout my education. During my time in both Riverside and San Diego I will treasure time spent with all of you.

Thoughts go out to those I had the pleasure to meet: Aholibama, Alan, Amos, Bastien, Bruno, Conor, Daniela, Desiree, Emrah, Eugenia, Fred, Glen, Gregorio, Janell, Jean, Jesse, Johanna, Maël, Max, Maria, Olivier, Pauline, Shigeru, Takayoshi, Xiao-Yu, and Xingbang.

When I first started the lab, my desk was in the same office as three of the most talented chemists I have met. Right next to me was Rei, and I could tell from the start he was extremely gifted. He was very kind to me, and I learned several tricks from his vast knowledge of experimental techniques. Daniel M. is definitely the most kindhearted chemist I met, always a great time with him around. Gaël was the final member of this talented group. There have been too many crazy moments to recount with Gaël, from banana throws to Futlab to late night Jungle Speed, but his advice is what impacted me the most. I definitely improved by being around him and picking up bits of knowledge, from lab techniques to learning "how to sell wind." I wish the best to all three of you in your future endeavors; it was a pleasure sharing the same lab space.

When I first met Martin, I knew we would get along very well. It was always nice to have someone in lab that you could talk to about anything. His knowledge of a wide range of musical styles always impressed me. I will never forget the non-stop laughter that happened whenever we would meet outside the lab. Thanks for always being a friend.

Without a doubt, Caleb was the best roommate I had during my graduate studies. The hilarious stories he told were always a treat after a long day of work. I have lots of great memories, and gained valuable advice from him. Best wishes on your independent career Prof. C.

With Fatme, there were lots of good conversations over afternoon coffee or dinner. Thanks for your help with solving disordered crystal structures and other chemistry related problems.

There are very few people that really alter your perception and have a significant impact on your life. Without a doubt, Cory is one of those people to me. In lab, the way he fundamentally thought about chemistry was inspiring. His enthusiasm for helping others is unrivaled. Outside the lab, Cory is always a blast to be around and I definitely have had some of the best times of my life going to events he recommended. Thanks for all the laughs, spectacular food recommendations, and awesome memories.

Daniel “Jimmy” also contributed to these life-changing events. I will never forget his willingness to try new things and hidden wild side. Seeing one of our favorite bands, AC/DC, was one of the best experiences that I will cherish forever. We have the most random conversations (conver-SAY-SHIONS), and I will never forget the “TBH” and “BTW” moments. Thanks for everything, especially with proofreading.

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David W. was always a blast to be around. I have fond memories of times spent at your place in Riverside, usually with quite a bit of drinks involved and once with stinky cheese. The nights out, featuring many drinks as well, are unforgettable, well as much as can be remembered. Thanks for the fun times.

In the middle of my PhD the lab migrated to San Diego and Matt Del Bel, a student from a neighboring lab, made a huge effort in welcoming me and eventually became a very good friend. Thanks for your help with the organic aspects of my project, slow-cooker recipes, and fun memories.

I have been very lucky to be part of a lab that attracts many international scholars. Every German researcher that has come by the lab has left as a cherished friend to me.

The first German I had the pleasure to meet was Fabian *"Whaaaaaat"* Dielmann. Experimentally, he was top notch and I learned a lot from simply watching him. When I was homeless for a week in between apartments, he and his family welcomed me to stay with them. Living with Fabian and his wife Tania, son Samuel, and newborn Nora was a quaint experience. Thank you Tania for all the delicious meals and the Dielmann family for the hospitality. Best wishes to your independent career and your delightful family.

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Having Dominik and Domenik at the same time was quite confusing, so Big Dom and Baby Dom titles were created. Thanks Big Dom for the coffee discussions and your valuable comments when proofreading my drafts. Thanks Baby Dom for joining in on the adventures in your short period here, especially the endless taco and beer events.

There is so much I can say about Steffen “Stttttttyyyyyyyyrrrrrraaaaaa.” I cherish our adventures around San Diego, Los Angeles, and even down to Mexico. It was always a pleasure having a beer and schnitzel, and I cannot wait to share some again in Germany.

As soon as I met Florian I knew we were instant friends. In his short stint, we shared many nice moments. Our nights out on the town were always a blast, both in San Diego and in Germany. Thank you for hosting me on my first ever trip to Europe. I really appreciate the time you took to show me around. You are always welcome wherever I am, my friend.

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Melaimi, G. Bertrand, *Chem. Commun.* **2014**, 2014, *50*, 7837–7839. The dissertation author was the primary investigator of these papers.

Chapter 2 has been adapted from materials published in R. Kretschmer, D. A. Ruiz, C. E. Moore, A. L. Rheingold, G. Bertrand, *Angew. Chem. Int. Ed.* **2014**, *53*, 8176–8179 and L. Liu, D. A. Ruiz, F. Dahcheh, G. Bertrand, *Chem. Commun.* **2015**, *51*, 12732–12735. The dissertation author was co-primary investigator of these papers.

Chapter 3 has been submitted for publication. L. Liu, D. A. Ruiz, G. Bertrand, "A Room Temperature Stable Singlet Phosphinidene," *Nature Chem.* The dissertation author was co-primary investigator of this paper.

VITA

Education

Ph.D. in Chemistry **2012 - 2015**

University of California, San Diego (Advisor: Professor Guy Bertrand)

M.S. in Chemistry **2010 - 2012**

University of California, Riverside (Advisor: Professor Guy Bertrand)

B.A. in Chemistry with Honors **2006 - 2010**

California State University, San Bernardino

Publications

- L. Liu, **D. A. Ruiz**, F. Dahcheh, G. Bertrand, "Isolation of a Lewis base stabilized parent phosphenium (PH_2^+) and related species" *Chem. Commun.* **2015**, *51*, 12732.
- **D. A. Ruiz**, M. Melaimi, G. Bertrand, "An efficient synthetic route to stable bis(carbene)borylenes [(L_1)(L_2)BH]" *Chem. Commun.* **2014**, 2014, *50*, 7837.
- R. Kretschmer, **D. A. Ruiz**, C. E. Moore, A. L. Rheingold, G. Bertrand, "One, Two, and Three Electron Reduction of a CAAC-$SbCl_3$ Adduct" *Angew. Chem. Int. Ed.* **2014**, *53*, 8176.
- **D. A. Ruiz**, M. Melaimi, G. Bertrand, "Carbodicarbenes, Carbon(0) Derivatives, Can Dimerize" *Chem. Asian J.* **2013**, *8*, 2940.
- **D. A. Ruiz**, G. Ung, M. Melaimi, G. Bertrand, "Deprotonation of a Borohydride: Synthesis of a Carbene-Stabilized Boryl Anion" *Angew. Chem. Int. Ed.* **2013**, *52*, 7590.

Presentations

- "A room temperature stable singlet phosphinidene" D. A. Ruiz, L. Liu and G. Bertrand, 45th Western Regional ACS Meeting, November 6-8, 2015, San Marcos, CA (*oral*).
- "Carbenes Stabilizing Unusual Boron and Antimony Species" D. A. Ruiz and G. Bertrand, 2014 SACNAS National Conference, October 16-18, 2014, Los Angeles, CA. *(oral)*
- "Exploring novel carbodicarbenes: Stability and reactivity" D. A. Ruiz and G. Bertrand, 248th ACS National Meeting & Exposition, August 10-14, 2014, San Francisco, CA. *(oral)*

- “Synthesis and reactivity of stable nucleophilic boron species” D. A. Ruiz and G. Bertrand, 247th ACS National Meeting & Exposition, March 16-20, 2014, Dallas, TX. *(oral)*
- “Synthesis of Bent Allenes and their use as Ligands for Transition Metal Catalysts” D. A. Ruiz, M. Melaimi and G. Bertrand, SCCUR, November 21, 2009, CSU, Dominguez Hills. *(poster)*

Awards

- **US Department of Education GAANN fellowship 2013-2015**: A fellowship awarded to provide rigorous and integrated research and teaching experiences to prepare students to assume post-graduate leadership roles in chemical research and education. Included an annual stipend of $27,000 as well as an additional $2,500 in travel and research support funds.
- **Travel Awards 2014**: ACS Award to attend the 248th ACS National Meeting & Exposition in San Francisco, CA and UCSD Award to attend the 247th ACS National Meeting & Exposition in Dallas, TX.
- **UCR Dean's Distinguished Fellowship 2010-2012**
- **CSU-LSAMP Student Scholar 2009-2010**: Awarded to students who face or have faced social, educational, or economic barriers to careers in STEM. Included support of $2,500 for student involvement in activities that enhance graduate school readiness.
- **ACS Most Outstanding Inorganic Chemistry Student Award at CSUSB 2010**

Technical Skills

- Expert at synthesizing and handling air and moisture sensitive compounds (Schlenk and glovebox techniques).
- Operation of several analytical instruments, including NMR (^{1}H, ^{13}C, ^{11}B, ^{19}F, ^{29}Si, ^{31}P), MS, IR, GC, UV-Vis.
- Setting up single crystal X-ray diffraction data collection and intermediate knowledge of solving of data sets.
- Able to read, write, and speak English and Spanish fluently.

Teaching Experience

- **Certification of The College Classroom 2014**: A seminar style course that aims to give a strong foundation in the constructivist theory of learning and how to integrate that pedagogy into an active, student-centered class
- **Teaching Assistant 2010-2013**: UCSD & UCR: Introductory General and Organic Chemistry Discussions and Laboratories

ABSTRACT OF THE DISSERTATION

Stabilization of Highly Reactive Group 13 and 15 Species

by

David Anthony Ruiz

Doctor of Philosophy in Chemistry

University of California, San Diego, 2015

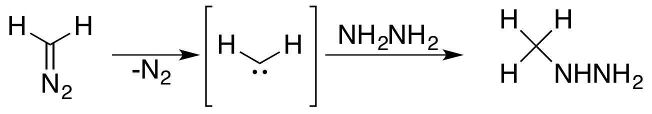
Professor Guy Bertrand, Chair

Carbenes have a long history of being classed as highly reactive species, whose isolation was deemed impossible. However, a paradigm shift occurred over two decades ago when the first stable carbene was reported. Since then, the field of stable carbene chemistry has flourished and applications in numerous fields of chemistry have been found. One unlikely application comes from their ability to act as stabilizing entities. Indeed, a wide variety of previously unattainable transition metal and main group species have been isolated via carbene stabilization. In this manuscript, carbenes will be utilized to isolate highly reactive species based on Group 13 and 15 elements. The first part of

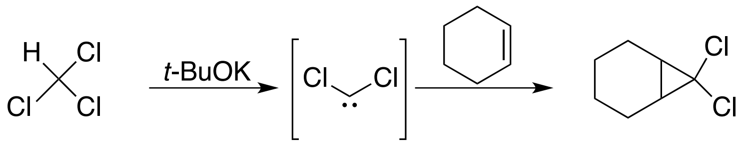
this manuscript will describe the design and synthesis of boron centered nucleophiles supported by carbenes. Then, it will be shown that the steric environment of the carbene plays a pivotal role in protecting highly reactive phosphenium fragments. The electronic properties of carbenes are also a crucial characteristic to consider and we demonstrate that with the appropriate carbene framework, antimony species can be stabilized in several oxidation states. Finally, we will demonstrate that a phosphinidene, the phosphorus analogue of carbenes, which has eluded isolation so far, can be stabilized with the appropriate framework.

General Introduction

Current chemical understating sets a paradigm on what is considered unusual or highly reactive. Accordingly, before the octet rule was established, chemists attempted to prepare molecules that are now considered non-viable. As early as 1835, Dumas sought to dehydrate methanol and generate the methylene carbene (:CH_2).[1] Carbenes are defined as neutral molecules featuring a divalent carbon atom, which only possesses six electrons in its valence shell. After the early attempts, carbenes were soon considered too reactive to be isolated and were only postulated as intermediates in a variety of chemical transformations. Pioneering studies at the end of the 19th century and beginning of the 20th century by Curtius[2] and Staudinger[3] demonstrated that carbenes could be generated from diazo compounds and ketenes (Scheme I.1), and that they were indeed very reactive species. Their application as organic synthons was made popular by the discovery of the cylcopropanation reaction by Doering[4] in the middle of the 20th century.



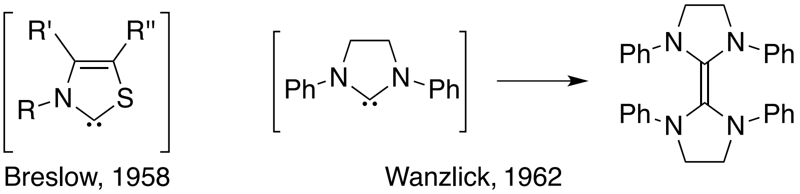
Staudinger, 1912



Doering, 1954

Scheme I.1: Early studies on transient carbene species.

At the end of the 50s, Breslow[5] and Wanzlick[6] proposed the idea of persistent singlet carbenes. They demonstrated that the presence of nitrogen atoms around the carbene center could drastically improve its stability, due to mesomeric effects. However, these carbenes could still not be isolated, and Wanzlick only obtained the dimerization product (Scheme I.2).



Scheme I.2: Postulated singlet carbenes.

While the search for stable carbenes was ongoing, several groups reported on transition metal carbene complexes. The groups of Fischer,[7] Öfele,[8] Lappert,[9] Wanzlick,[10] and Schrock[11] demonstrated that a variety of carbene fragments could be coordinated to metal centers (Figure I.1). Although the free carbenes could not be isolated, the complexes provided a foundation for the ubiquitous use of carbenes as ligands for transition metals today.[12]

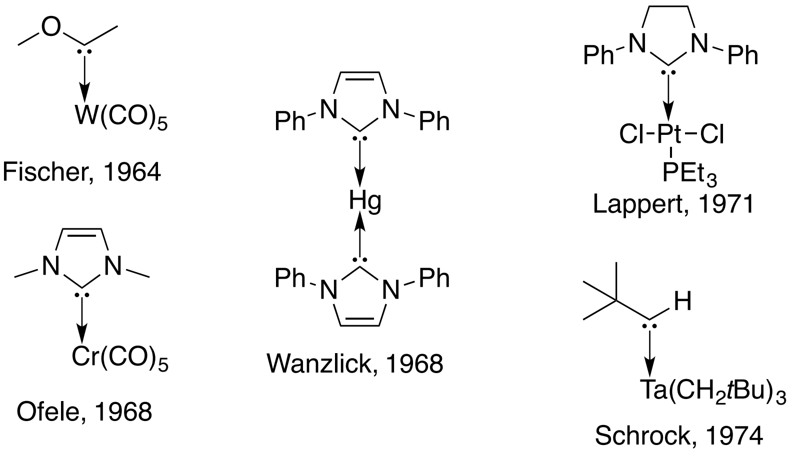
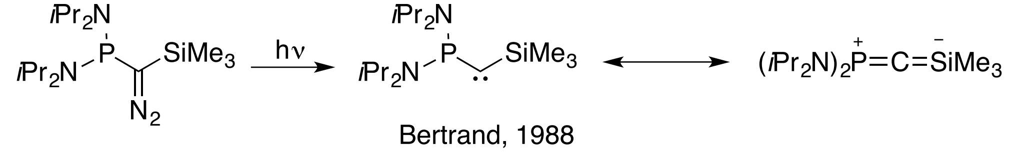


Figure I.1: The first stable carbene-metal complexes.

The pursuit eventually came to an end in 1988 when Bertrand and co-workers reported on the isolation of a stable carbene.[13] The (phosphino)(silyl)carbene was generated by liberation of molecular nitrogen from the diazo precursor (Scheme I.3). The decoration around the carbene center is what gives this species its stability. A push-pull system was designed, with the phosphorus atom "pushing" electron density into the empty orbital of carbene center and the silicon atom "pulling" electron density away from the carbene lone pair. Thus, a resonance involving an alkene-like structure contributes to the structure. Nonetheless, its reactivity mimics that of "classical" carbenes.[14]



Scheme I.3: Synthesis of the first stable carbene.

Three years after that seminal discovery, Arduengo reported on an *N*-heterocyclic carbene (NHC) that was crystalline (Figure I.2), allowing for structural characterization by X-ray crystallography.[15] This carbene was reported to be indefinitely stable at room temperature under an inert atmosphere, making it bottleable. Unlike the acylic push-pull carbene of Bertrand, the incorporation into a five-membered ring for NHCs gave them an acute bond angle around the carbene center. This leads to robust transition metal complexes with NHCs in comparison to poor coordination and limited applications for acyclic carbenes.[16] Indeed, transition metal-NHC complexes have found widespread use.[14]

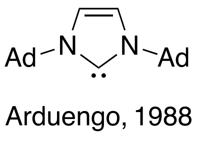
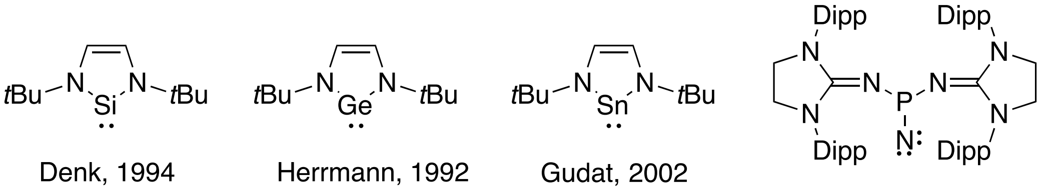


Figure I.2: The first stable *N*-heterocyclic carbene.

Since these two groundbreaking findings, the field of stable carbene chemistry has flourished. Many different derivatives have been reported with varying heteroatom substituents, steric properties, and electronic properties.[17] Soon after the first stable carbenes, heavier group 14 analogues were also shown to be stable (Figure I.3),[18] with reports on silylenes,[19] germylenes,[20] and stannylenes.[21] Only recently a stable nitrogen analogue, namely a nitrene, was reported.[22] However, the carbene analogues of heavier Group 15 elements still elude isolation.



Denk, 1994 Herrmann, 1992 Gudat, 2002 Bertrand, 2012

Figure I.3: The stable heavier carbene analogues and a stable nitrene.

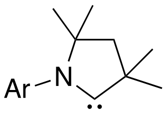
Carbenes and their analogues can exist in two electronic states.[23] The singlet state features a filled and vacant orbital, while a triplet carbene possesses two singly occupied orbitals (Figure I.4). Thus, singlet carbenes should have ambiphilic reactivity while triplet carbenes behave as diradicals. The carbene ground state multiplicity therefore has a decisive impact on the stability and reactivity of the carbene. For example, the vast derivatives of stable carbenes mentioned above all feature singlet states, while triplet carbenes are so far only short lived species.[24]

Singlet Triplet

Figure I.4: Representation of a singlet and triplet carbene.

As mentioned above for the (phosphino)(silyl)carbene, the push-pull substitution pattern favors the singlet state and allows it to be stable. In the case of the NHC, the nitrogen atoms around the carbene center act as both π-donors and σ-attractors, which stabilizes the singlet state. The donation of the two nitrogen lone pairs fills the formally vacant orbital on the carbene while the electron-withdrawing inductive effect of the electronegative nitrogen atoms stabilizes the lone pair on the carbene.

NHCs were known to be potent nucleophiles due to the presence of the lone pair on the carbene center. However, the presence of two π-donating nitrogen atoms around the carbene center fills the vacant orbital and diminishes its ambiphilic nature. However, the electrophilic properties of carbenes were made apparent by the isolation of the cyclic(alkyl)(amino) carbene (CAAC)[25] and its ensuing reactivity.[26] By replacing one of the π-donating and σ-withdrawing nitrogen atoms by a quaternary carbon that is σ-donating but incapable to π-donate, an enhancement of both the nucleophilicity and electrophilicity of the carbene occurs compared to NHCs. This modification allows CAACs to behave differently to NHCs. A groundbreaking example is the ability of CAACs to mimic transition metals[27] by splitting dihydrogen and ammonia under mild conditions,[28] whereas NHCs are unable to. This ambiphilic nature of CAACs has led to a variety of small molecule activation.[27, 29]



Bertrand, 2005

Figure I.5: A cyclic(alkyl)(amino) carbene.

Stable carbenes have versatile reactivity and one area they have impacted is the field of isolating highly reactive species.[30] With transition metals, CAACs have been utilized to stabilize them in previously unknown oxidation states, especially in the formal zero oxidation state.[17c] In the field of main group chemistry, carbenes have had a tremendous impact. With the help of carbenes, the isolation of numerous compounds that can be viewed as formal complexes of soluble allotropes of main group elements could be realized,[31] and further transformations into other oxidation states could be achieved.[32] For example, while diatomic nitrogen is a very stable allotrope, its heavier P_2 counterpart has eluded isolation. However, it was shown to be perfectly stable as the corresponding $(carbene)_2P_2$ complex (Figure I.6).[33] Further chemistry on this complex allowed for the isolation of the previously unknown P_2O_4 fragment via carbene stabilization.[34] Another noteworthy example is the isolation of the first ever crystallographically characterized compound containing a BB triple bond (Figure I.6).[35] The carbene stabilization allows this compound to be stable under ambient conditions.

Robinson, 2008

Braunschweig, 2012

Figure I.6: A diatomic phosphorus molecule and the first crystalline BB triple bond, both stabilized by NHCs.

There has been a paradigm shift over the last decade when considering the types of main-group species that can be isolated, and this is in large part due to the peculiar stabilizing effects of persistent carbenes. In this manuscript, we will describe the isolation of unusual molecules previously thought to be unstable or too highly reactive, using carbenes as the stabilizing entities. Chapter 1 will focus on the development of boron-centered nucleophiles supported by carbenes. In Chapter 2, the appropriate carbenes will be deliberately selected according to their steric and electronic properties to isolate novel compounds based on Group 15 elements. Finally, in Chapter 3, we demonstrate that the phosphorus analogue of carbenes, namely a phosphinidene, which was considered as a highly reactive species, can be isolated under ambient conditions.

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Chapter 1:

Synthesis of Nucleophilic Tricoordinate Boron Compounds

Introduction

Boron hydrides and boron derived Lewis acids are ubiquitous reagents in organic and inorganic synthesis.[1] Trivalent boron compounds are typically strong acids, because they formally have only six valence electrons and therefore do not fulfill the octet rule. Due to this property, the idea of bottleable, nucleophilic, trivalent-based boron reagents seemed unrealistic. However, Yamashita, Nozaki, and co-workers shattered this belief in 2006 with the isolation and structural characterization of the boryl-lithium **1.A**[2] (Figure 1.1). They demonstrated that **1.A** indeed behaves as a boron-based nucleophile.[3] Since then, several other boron-centered nucleophiles have been reported.[4] Braunschweig *et al.* isolated two unique types of boron nucleophiles **1.B**[5] and **1.C**[6] (Figure 1.1), which feature a π-nucleophilic and sp-hybridized boron atom, respectively. The NHC-stabilized parent boryl anion **1.D** was also reported by Curran *et al.*; although it could not be isolated, they did trap it with a variety of electrophiles proving the transient existence of **1.D**.[7] The first doubly negatively charged boron-centered nucleophile **1.E** was reported by Bernhardt *et al.*[8] This dianion was also shown to react with electrophiles, proving its nucleophilic nature at the boron center.[9] These aforementioned compounds all share the motif of being negatively charged. Yet in 2011, a milestone was reached in our lab when the first neutral, nucleophilic, tricoordinate boron derivative **1.F** was isolated and fully characterized[10] (Figure 1.1). This compound is isoelectronic with amines and phosphines, which gives it the potential to behave as a unique ligand framework for transition metals.[11] Unfortunately, the steric environment around the boron center of **1.F** hampered its reactivity from any electrophile larger than a proton.

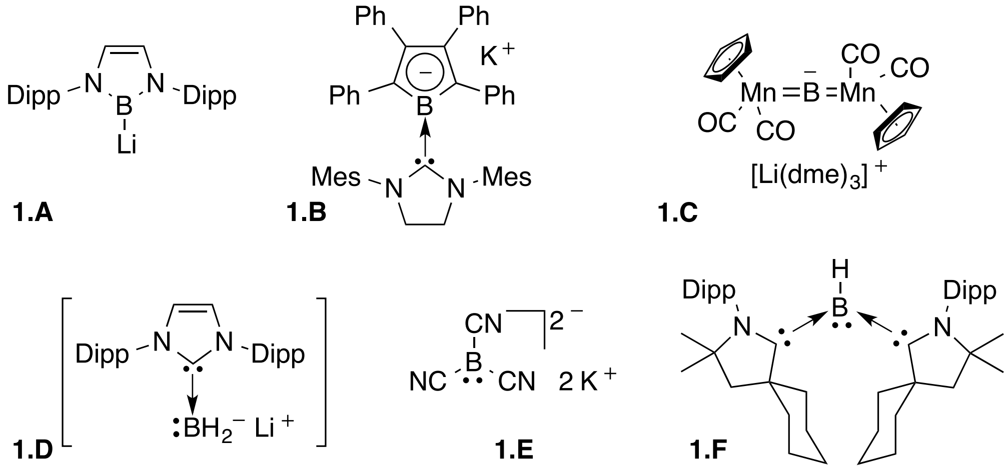
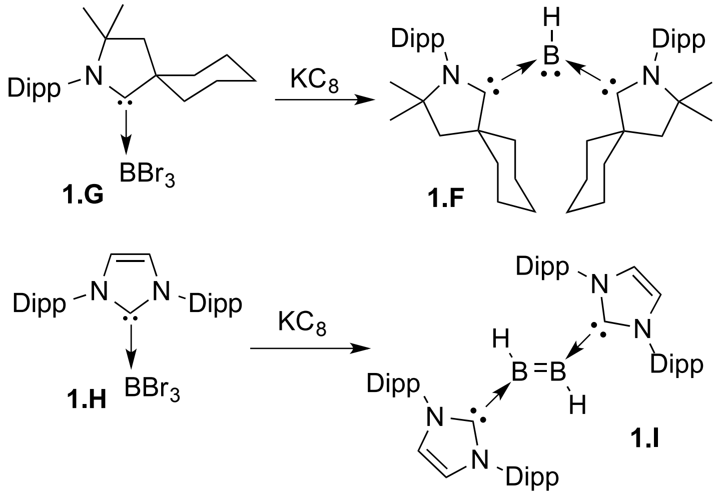


Figure 1.1: Known nucleophilic boron compounds **1.A-F**.

In this chapter, we describe an improved and more versatile synthesis for neutral tricoordinate boron nucleophiles, as well as a novel synthetic approach to generate boryl anions. The boron-based nucleophilic character of these compounds will be exemplified.

A) Neutral tricoordinate boron nucleophiles

Compound **1.F** was prepared by reduction of the CAAC-BBr_3 adduct **1.G** with excess KC_8 (Scheme 1.1). This synthetic route afforded **1.F** in just 33% yield, is far from being understood, and certainly does not have a broad scope. By merely switching from a CAAC to the NHC analogue, the outcome is entirely different. Robinson *et al.* reported that the reduction of the NHC-BBr_3 adduct **1.H** with excess KC_8 leads to dimers of type **1.I**, among other compounds[12] (Scheme 1.1). Moreover, this synthetic pathway limits the decoration of the boron center. Installing two different carbenes would allow for a fine tuning of the electronic properties of the boron center. Additionally, the hydrogen source of the B–H moiety is speculated to result from hydrogen abstraction of the solvent, due to the strong reducing conditions.[13] Therefore, a stepwise and controlled reduction appears to be a promising synthetic strategy.

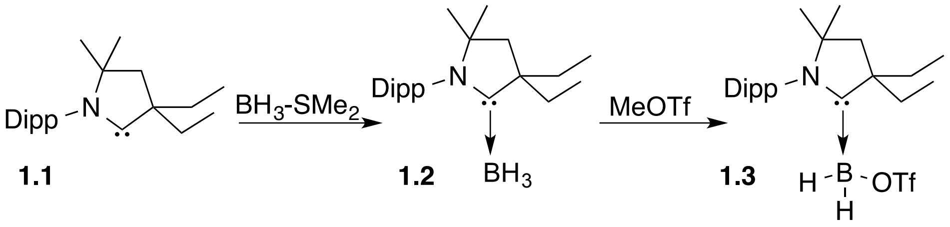


Scheme 1.1: Synthetic route to compound **1.F** from **1.G**, and the analogous reaction with an NHC yielding **1.I** instead.

We envisaged a synthetic route where the carbenes could be introduced sequentially, yielding a precursor whose reduction could be more controlled. Since CAACs have already proven their ability to stabilize neutral tricoordinate boron nucleophiles, we wanted to first start with a CAAC-borane adduct. To begin the synthesis, the boron was installed onto the CAAC by reaction of the free carbene **1.1** with a solution of BH_3–SMe_2 complex (Scheme 1.2). After work-up, **1.2** was obtained as a colorless solid in 96% yield. The ^{11}B NMR spectrum shows a quartet at –28.5 ppm due to the coupling between the three hydrogen atoms bound to the boron (J_{BH} = 87.5 Hz).

Curran *et al.* demonstrated that the hydrogen atoms on carbene-borane compounds could be transformed into a variety of leaving groups.[14] With the appropriate leaving group on boron, carbenes can be introduced. The trifluoromethanesulfonate ($^{-}$OTf) anion is an excellent candidate as it is a weakly binding ligand that is readily displaced by nucleophiles. The reaction of **1.2** with methyl trifluoromethanesulfonate afforded CAAC monotriflate borane **1.3** in 95% yield as a colorless powder (Scheme

1.2). The ^{11}B NMR spectrum displays a broad signal at –6.1 ppm, which is shifted downfield from **1.1** (–28.5 ppm), and the ^{19}F NMR spectrum shows a singlet at –76.2 ppm, which is indicative of a triflate group covalently bound to boron. To ascertain the structure, colorless single crystals suitable for an X-ray diffraction study were obtained by vapor diffusion of pentane into a saturated chloroform solution. The solid-state structure of **1.3** confirmed the covalent nature of the triflate group (Figure 1.2).



Scheme 1.2: Synthesis of **1.3** starting from free carbene **1.1**.

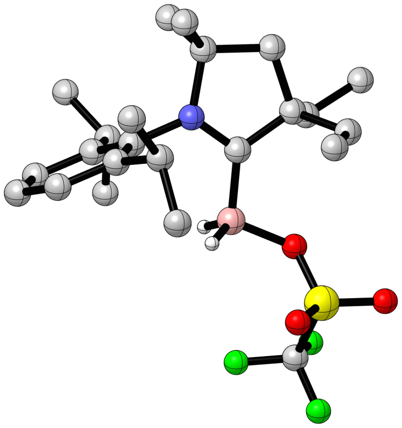
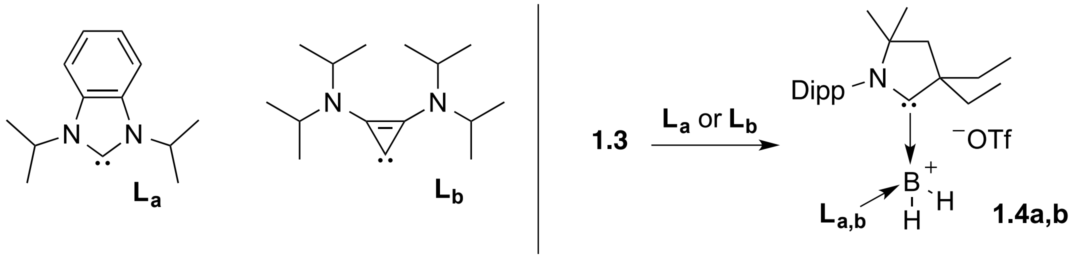


Figure 1.2: Molecular view of **1.3** in the solid state with hydrogen atoms (except B–H) omitted for clarity.

With this compound in hand, the next step was to displace the triflate group with a different carbene. Two carbenes were selected for this study, namely the benzimidazole-based NHC $\mathbf{L_a}$[15] and the cyclopropenylidene $\mathbf{L_b}$[16] (Scheme 1.3). These carbenes are relatively small and are very weak π-acceptors, so the synthesis of the products would demonstrate that a single CAAC is sufficient to stabilize the borylene. **1.3** reacted with both carbenes affording the desired bis(carbene) boronium salts **1.4a,b**, which were isolated as colorless solids in 95 and 80% yield, respectively. The OTf groups are no longer covalently bound as evidenced by the ^{19}F NMR spectra (**1.4a** = –78.0 ppm; **1.4b** = –79.3 ppm), and the ^{11}B NMR spectra display upfield well-defined triplets (**1.4a** = –28.6 ppm, J_{BH} = 82.9 Hz; **1.4b** = –27.7 ppm, J_{BH} = 87.9 Hz). These compounds are very robust, and do not decompose upon exposure to air or moisture. The deprotonation or reduction of these species would lead directly to the desired bis(carbene)borylene compound. Unfortunately, all attempts to obtain the desired neutral tricoordinate boron derivatives from **1.4a,b** failed.



Scheme 1.3: Left: Benzimidazolylidene $\mathbf{L_a}$ and cyclopropenylidene $\mathbf{L_b}$. Right: Synthesis of compounds **1.4a,b**.

To circumvent this letdown, a second hydrogen atom bound to boron was replaced by a triflate group, which is more capable of being reduced. Treatment of **1.4a,b** with HOTf leads directly to **1.5a,b**, which were isolated as solids in 70 and 67% yield, respectively. Once one OTf is bound again, the ^{11}B NMR spectra display broad downfield shifts (**1.5a** = –7.5 ppm; **1.5b** = –5.1 ppm) compared to **1.4a,b**. Bound and free triflate groups are indicated by the two peaks observed in the ^{19}F NMR spectra (**1.5a** = –75.4, –78.1 ppm; **1.5b** = –76.2, –78.0 ppm). The ^{1}H NMR spectra become quite convoluted, probably because of the steric hindrance, which prevents rotation around the boron–carbon bonds. To make more crystalline products, the corresponding $^{-}BPh_4$ salts were obtained by anion exchange with $NaBPh_4$. The solid-state structures confirmed the connectivity around boron (Figure 1.3). These compounds are extremely robust, as a water wash is performed during work-up.

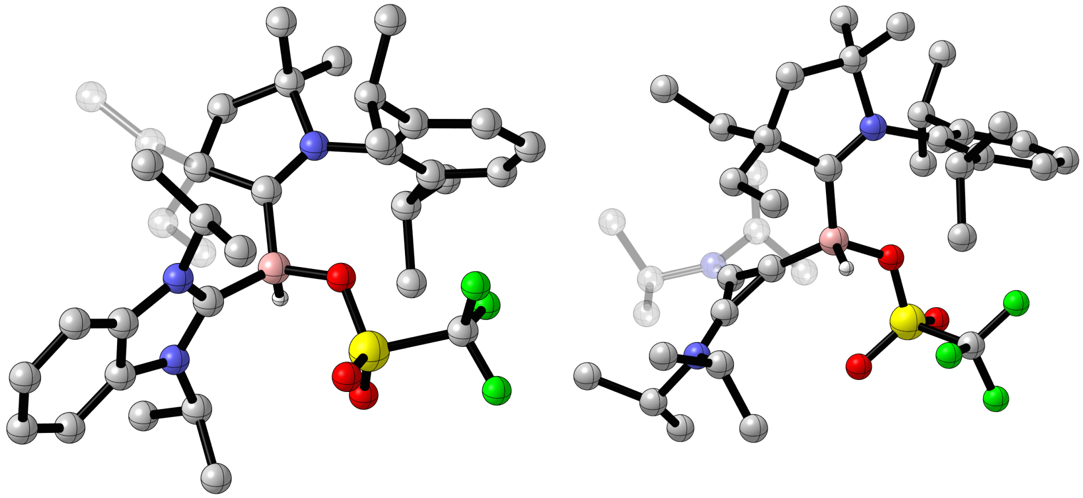
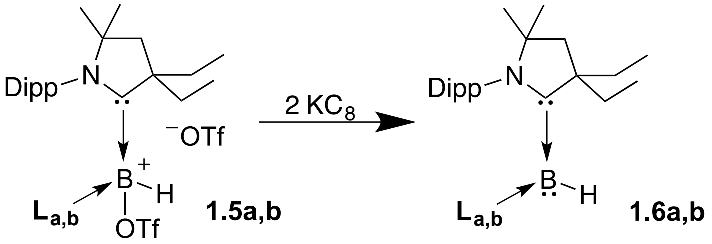


Figure 1.3: Molecular view of **1.5a** (left) and **1.5b** (right) in the solid state with hydrogen atoms (except B–H) and anions omitted for clarity.

As before, attempted deprotonation did not result in any chemical transformation. Fortunately, reduction attempts were fruitful. Mixing **1.5a,b** with two equivalents of KC_8 in THF lead to intense blue and red colored solutions, respectively. After workup, the desired neutral tricoordinate boron compounds **1.6a,b** were isolated in 87 and 82% yield, respectively (Scheme 1.4). These compounds are extremely sensitive to air and moisture, but can be stored under an inert atmosphere at room temperature without any signs of decomposition. Compared to the precursors, the ^{1}H NMR spectra are simplified since the boron center is no longer chiral. The ^{11}B NMR spectra display doublets at –1.3 (J_{BH} = 82.4 Hz) and 0.8 ppm (J_{BH} = 89.7 Hz) for **1.6a** and **1.6b**, respectively. Interestingly, these signals appear at higher field compared to **1.F** (+12.5 ppm), which can be attributed to the inferior π-acceptor properties of benzimidazolylidene **L$_a$** and cyclopropenylidene **L$_b$** compared to CAACs.[17]



Scheme 1.4: Synthesis of neutral tricoordinate boron derivatives **1.6a,b** by reduction of **1.5a,b** with KC_8.

In order to analyze the structural parameters, single crystals of **1.6a** and **1.6b** suitable for X-ray diffraction studies were grown from concentrated pentane solutions (Figure 1.4, top). The B1–C2 bond lengths [**1.6a**: 1.572(2); **1.6b**: 1.5521(17) Å] are in the range typically observed for B–C single bonds. However, the B1–C1 bond is much shorter [**1.6a**: 1.462(3); **1.6b**: 1.4692(16) Å] and falls in the range of B–C double bonds.[18] Concurrently an elongation of the C1–N1 bond [**1.6a**: 1.418(2); **1.6b**: 1.4262(15) Å] occurs compared to that of the salt precursors [**1.5a**: 1.307(2); **1.5b**: 1.297(5) Å]. These structural parameters show that the formal boron lone pair is mainly delocalized over the CAAC ligand, with little over the second carbene. This is confirmed by DFT calculations, as can be seen from the HOMO diagrams (Figure 1.4, bottom).

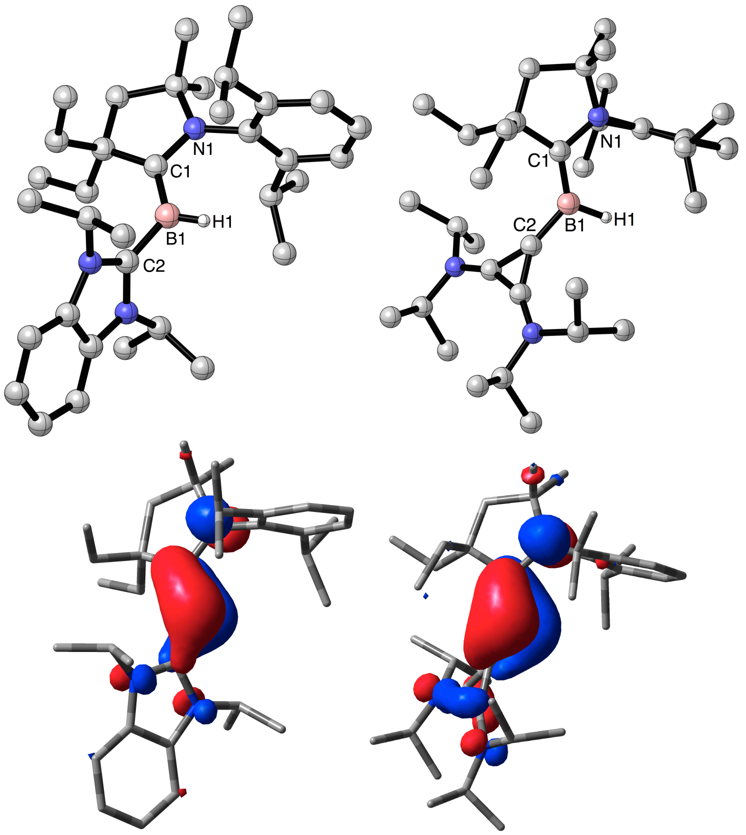
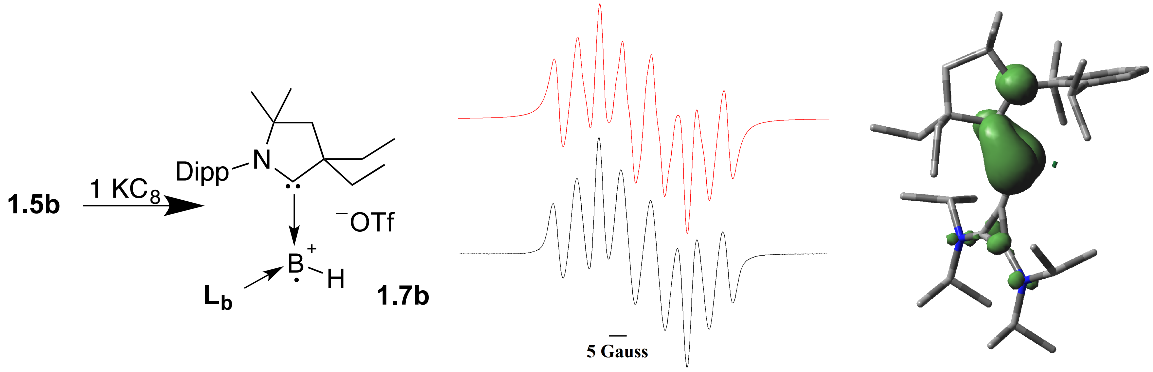


Figure 1.4: Top: Molecular view of **1.6a** (left) and **1.6b** (right) in the solid state with hydrogen atoms (except B–H) and solvent molecules omitted for clarity. Bottom: HOMO diagrams for **1.6a** (left) and **1.6b** (right) [BVP86/6-311+g(2d,p) level of theory].

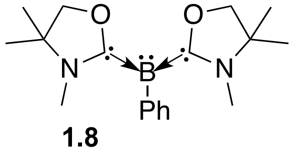
This delocalization allows these types of compounds to be stable, yet the boron center of **1.6a,b** is electron rich. Both compounds readily react with triflic acid, leading to the conjugate acids **1.4a,b**. Furthermore, adding only one equivalent of KC_8 to a solution of **1.5b** leads to persistent radical **1.7b** (Scheme 1.5, left). The room temperature EPR spectrum of **1.7b** (Scheme 1.5, middle) displays couplings with boron [a(^{11}B) = 4.994 G], hydrogen [a(^{1}H) = 10.065 G], and only one nitrogen nucleus [a(^{14}N) = 6.627 G]. DFT calculations confirm that the spin density distribution is manly delocalized over the CAAC and BH fragments, with very little contribution by carbene $\mathbf{L_b}$ (Scheme 1.5, right).

This again supports the significant role that the CAAC ligand plays in delocalizing the unpaired electron.[19]

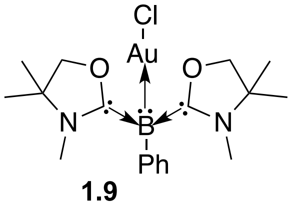


Scheme 1.5: Left: Synthesis of persistent radical **1.7b**. Middle: Simulated (top) and experimental (bottom) EPR spectra. Right: Spin density representation of **1.7b**. [(U)BVP86/6-311+g(2d,p) level of theory].

While these compounds are indeed neutral tricoordinate boron nucleophiles, these particular carbene decorations still seemed unsuitable to allow further chemistry to take place. This synthetic route does however pave the way for the preparation of a variety of bis(carbene)borylene adducts. In the same timeframe, Kinjo and coworkers reported derivative **1.8** (Figure 1.5, left), which features oxazol-2-ylidenes as the supporting carbene fragments.[20] This is significant because the steric environment around boron is immensely diminished compared to the bulky CAAC, as the Dipp functionality on the nitrogen is replaced by a methyl and an oxygen is adjacent to the carbene center. Kinjo and coworkers showed that their bis(carbene)borylene coordinates metals via the boron center, as exemplified by gold complex **1.9** (Figure 1.5, right). Even more spectacular, they demonstrated that complex **1.9** displayed good catalytic activity for the addition of X–H (X = N, O, C) bonds to alkynes.[21] This is the first report of a metal complex featuring a neutral boron-based ligand with applications in catalysis.



1.8



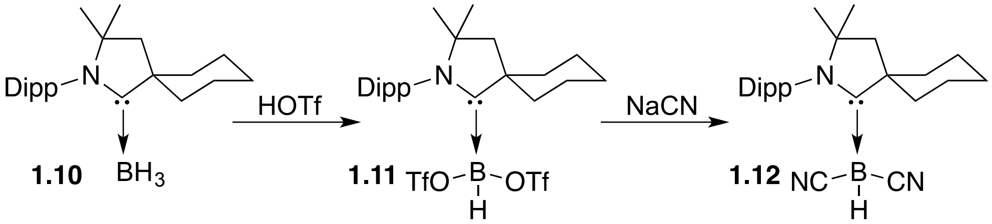
1.9

Figure 1.5: Boron centered nucleophile **1.8** and its gold complex **1.9**, isolated by the Kinjo lab.

B) Carbene-stabilized boryl anion

Although the aforementioned boron-based nucleophiles are neutral, most nucleophilic boron species tend to be anionic as exemplified by **1.A**–**1.E**. So far the syntheses of all these compounds (**1.A**–**1.F**, **1.6a,b**, and **1.8**) have been achieved by reduction of the boron halide or pseudo-halide precursor. For compound **1.A**, the authors commented that the attempted deprotonation of the precursor would lead to the formation of a Lewis acid-base adduct. Curran also noted that strong bases did not lead to boryl anion **1.D**. This can be explained by the intrinsic properties of the boron-hydrogen bond. The higher electronegativity of hydrogen (2.20) compared to boron (2.04) renders them as hydrides, making deprotonation an unreasonable synthetic approach. However, we reasoned that by decorating the boron center with the appropriate substituents, the boron-hydrogen bond could become acidic enough to be deprotonated by a strong base.

We targeted a carbene-stabilized boryl anion, with the carbene partner being a CAAC. As mentioned previously, CAACs are exceptional π-acceptors and this property will assist in the stabilization of the ensuing electron rich species. Furthermore, electron-withdrawing substituents at boron will favor deprotonation. Thus, OTf groups were first considered since they were successful in the previous synthesis. To maximize the acidic character of the B–H, we looked to install two OTf groups in one step. Gratifyingly, by reacting **1.10** with HOTf instead of MeOTf, the bis-(triflate) derivative **1.11** could be isolated in 80% yield (Scheme 1.6). Similarly to the mono-(triflate) analogue **1.3**, the ^{11}B NMR spectrum of **1.11** displays a broad signal at –2.2 ppm, which is upfield from **1.10** (–30.6 ppm). The ^{19}F NMR spectrum appears as a single signal at –76.2 ppm, indicating that both OTf groups are covalently bound. Single crystals suitable for an X-ray diffraction study were grown by vapor diffusion of pentane into a saturated chloroform solution of **1.11**. The solid-state structure confirmed the covalent nature of both the OTf groups to boron (Figure 1.6, left).



Scheme 1.6: Synthesis of **1.11** and **1.12** starting from carbene-borane **1.10**.

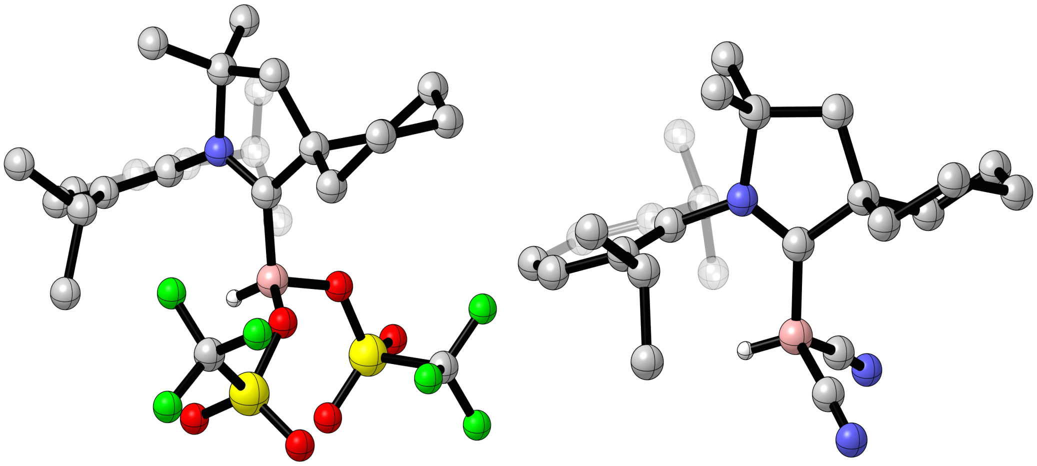


Figure 1.6: Molecular view of **1.11** (left) and **1.12** (right) in the solid state with hydrogen atoms (except B–H) omitted for clarity.

Disappointingly, the addition of strong bases to **1.11** did not lead to deprotonation. Seemingly, the B–H still retains hydridic character. Additionally, the steric environment around the boron center may kinetically encumber deprotonation, so stronger electron-withdrawing groups that are smaller could be installed help render deprotonation more favorable. To address both issues, the cyanide (CN^{-}) group appeared ideal. Reacting **1.11** with NaCN led to the displacement of the OTf groups, affording **1.12** in 87% yield (Scheme 1.6). The ^{11}B NMR spectrum appears as a doublet at –34.6 ppm (J_{BH} = 94 Hz) and no signal is apparent in the ^{19}F NMR spectrum. The structure was unambiguously determined by an X-ray diffraction study, showing bonding through the carbon of the nitrile ligand (Figure 1.6, right).

Reacting **1.12** with KHMDS led to a yellow colored solution. The ^{11}B NMR spectrum displayed an upfield peak at –17.9 as a singlet, indicating the absence of a B–H bond. The compound was isolated as a yellow solid in 95% yield and single crystals were grown from a concentrated THF solution. The X-ray diffraction study revealed that **1.12** was indeed deprotonated leading to the desired boryl anion **1.13**, showing a polymeric nature in the solid state (Figure 1.7).

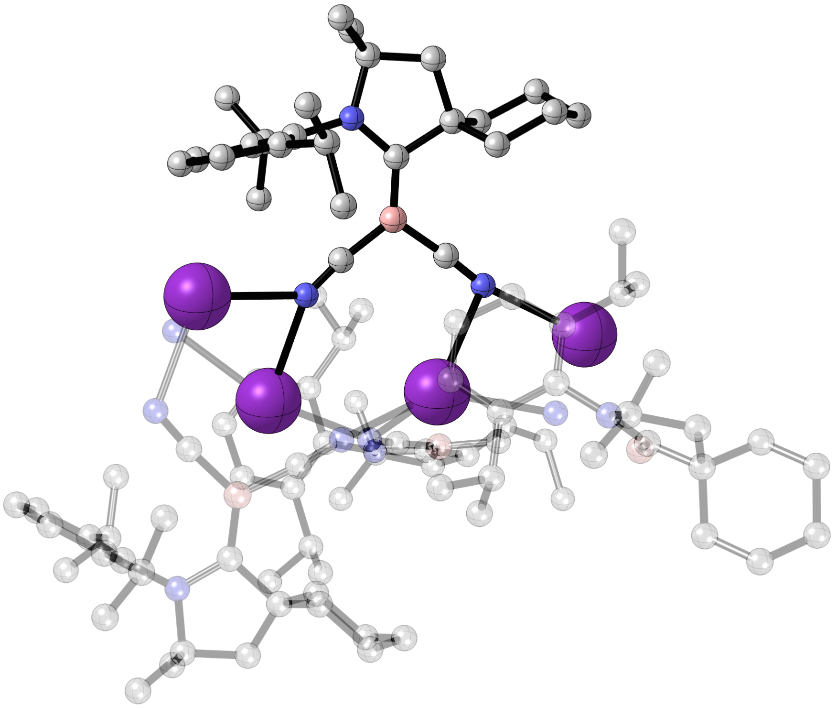


Figure 1.7: Molecular view of **1.13** in the solid state with hydrogen atoms and solvent molecules omitted for clarity. Only one of the polymeric CAAC units and the potassium cations are highlighted for clarity.

Treatment of **1.13** with dibenzo-18-crown-6 sequestered the potassium cation within the sphere of the crown ether, affording the monomeric boryl anion **1.14** (Figure 1.8). The B–$C_{nitrile}$ bond lengths in **1.14** (B1–C2: 1.553(2), B1–C3: 1.552(2) Å) are slightly shorter than in **1.12** (B1–C2: 1.605(6), B1–C3: 1.595(6) Å), but longer than in the dianion **1.E** (1.513 Å), which indicates a weaker delocalization of the negative charge on the nitrile groups. As before, the significant stabilizing role of the CAAC is apparent by the structural parameters of **1.4**. The B1–C1 bond distance (1.473(2) Å) is considerably shortened compared to **1.2** (1.617(6) Å), indicating the delocalization of electron density onto the CAAC. Concomitantly, the C1–N1 bond elongates from **1.12** (1.294(4) Å) to **1.14** (1.396(2) Å), and the boron adopts a trigonal planar geometry. These structural fluctuations demonstrate the important role of the π-accepting properties of the CAAC in stabilizing **1.14**.

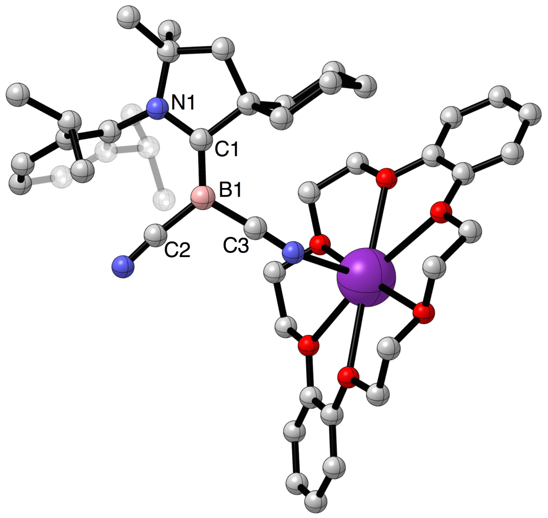
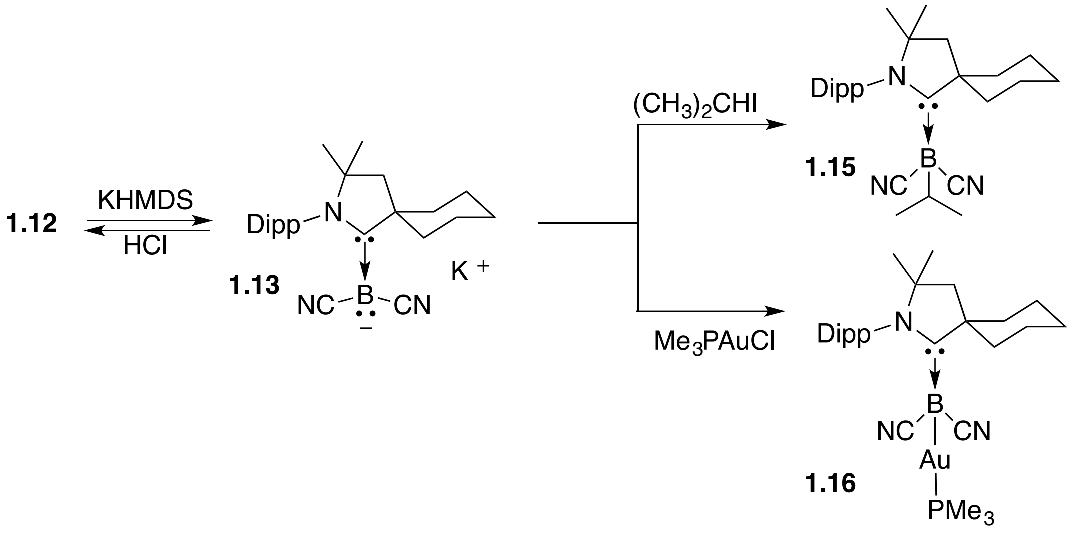


Figure 1.8: Molecular view of **1.14** in the solid state with hydrogen atoms omitted for clarity.

Boryl anion **1.13** is extremely sensitive to air and moisture, but it can be stored in the solid state and in solution under an inert atmosphere with no signs of decomposition. Upon reaction with HCl, **1.13** readily converts back to hydroborane **1.12** (Scheme 1.7).



Scheme 1.7: Synthesis and reactivity of boryl anion **1.13**.

To further test the nucleophilicity of the boron center, **1.13** was reacted with isopropyl iodide (Scheme 1.7). After work up, a new ^{11}B NMR signal appeared at higher field (–21.9 ppm) compared to **1.13**. This is shift is indicative of a four coordinate boron center. To confirm the structure, single crystals were obtained by vapor diffusion of hexanes into a saturated chloroform solution. The X-ray diffraction study of the crystals indeed displayed **1.15** (Figure 1.9, left), which is the product from the nucleophilic attack of boron to the electrophilic carbon of the alkyl halide.

To further verify the nucleophilic character at boron, **1.13** was reacted with Me_3PAuCl (Scheme 1.7). As before, the ^{11}B NMR spectrum displayed an upfield shift (–26.2 ppm) but the signal appeared as a doublet, due to the boron–phosphorus coupling (J_{BP} = 30 Hz). An X-ray diffraction study of the compound showed the boryl-gold complex **1.16** (Figure 1.9, right). The boron-gold bond has a length of 2.210(5) Å, and the B–C_{CAAC} bond elongates to 1.544 Å compared to **1.13**.

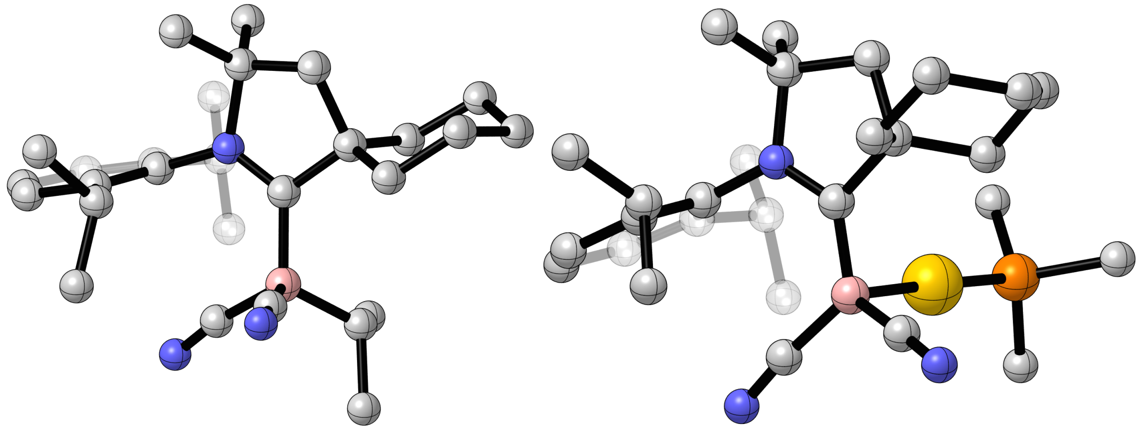


Figure 1.9: Molecular view of **1.15** (left) and **1.16** (right) in the solid state with hydrogen atoms and solvent molecules omitted for clarity.

Conclusion

In this chapter, we demonstrated new strategies to afford tricoordinate boron based compounds that behave as nucleophiles. One method involves a stepwise and versatile approach, while the other takes a radically new approach, namely deprotonating a hydroborane species. A variety of bis(carbene) borylene adducts can be now prepared, and fine tuning of the electronic environment can be achieved by simple carbene replacement. Since bis(carbene) borylene compounds are isoelectronic with amines and phosphines, they can similarly be used as ligands in catalysis. Kinjo already demonstrated with his system that they indeed have catalytic potential. These types of systems have a seminal trajectory and with continued progress, a series of boron-based ligands can become available to the synthetic community. In later efforts by our group[22] and others,[23] a series of other derivatives with unique properties have been reported.

Chapter 1 has been adapted from materials published in D. A. Ruiz, G. Ung, M. Melaimi, G. Bertrand, *Angew. Chem. Int. Ed.* **2013**, *52*, 7590–7592 and D. A. Ruiz, M. Melaimi, G. Bertrand, *Chem. Commun.* **2014**, 2014, *50*, 7837–7839. The dissertation author was the primary investigator of these papers.

Appendix: Experimental Section

1) General Information

All manipulations were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under argon. ^{1}H, ^{13}C, ^{11}B, ^{19}F and ^{31}P NMR spectra were recorded on a Varian VX 500, Bruker 300, and Jeol 500 spectrometer at 25 °C. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *sept* = septet, *m* = multiplet, *br* = broad signal. Chemical shifts are given in ppm and coupling constants *J* are given in Hz. EPR spectra were obtained using an X-band Bruker E500 spectrometer. Field calibration was accomplished by using a standard of solid 2,2-diphenyl-1-picrylhydrazyl (DPPH), g = 2.0036.[24] Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54178 Å) at the UC San Diego Crystallography Facility. Mass spectrometry was performed at the UC San Diego Mass Spectrometry Laboratory. Melting points were measured with an electrothermal MEL-TEMP apparatus.

2) Synthetic Procedures

Preparation of 1.2: The literature procedure was followed.[25] ^{1}H NMR (300 MHz, C_6D_6): δ = 7.25 (m, 2H), 7.15 (m, 1H), 2.87 (sept, *J* = 6.6 Hz, 2H), 2.05 (m, 2H), 1.94 (m, 2H), 1.63 (s, 2H), 1.58 (s, 3H, BH_3), 1.49 (d, *J* = 6.7 Hz, 6H), 1.24 (d, *J* = 6.6 Hz, 6H), 1.02 (s, 6H), 1.00 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (75 MHz, C_6D_6): δ = 145.6 (C_q), 134.3 (C_q), 129.3 (CH_{Ar}), 124.7 (CH_{Ar}), 76.1 (C_q), 60.9 (Cq), 41.5 (CH_2), 33.2 (CH_2), 29.7, 28.9, 26.1, 23.4, 9.6; ^{11}B NMR (96 MHz, C_6D_6): δ = –28.5 (q, J_{BH} = 87.5 Hz).

Preparation of 1.3: To a solution of **1.2** (4.0 g, 12.2 mmol) in 50 mL of benzene MeOTf (2.0 mL, 18.3 mmol) was added slowly, whereby bubbling occurred. The reaction was stirred overnight and the volatiles were removed under vacuum. The residue was washed with 60 mL of hexanes, and after drying under vacuum, **1.3** was isolated as a colorless solid (5.5 g, 95% yield). Colorless single crystals were obtained by vapor diffusion of pentane in a saturated chloroform solution. ^{1}H NMR (300 MHz, C_6D_6): δ = 7.10 (t, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 2H), 3.24 (br s, 2H, BH_2), 2.53 (sept, *J* = 6.6 Hz, 2H), 2.01 (m, 2H), 1.80 (m, 2H), 1.49 (s, 2H), 1.27 (d, *J* = 6.6 Hz, 6H), 1.06 (d, *J* = 6.6 Hz, 6H), 0.88 (t, *J* = 7.4 Hz, 6H), 0.82 (s, 6H); ^{13}C NMR (75 MHz, C_6D_6): δ = 144.6 (C_q), 132.1 (C_q), 130.3 (CH_{Ar}), 125.4 (CH_{Ar}), 78.6 (C_q), 62.1 (C_q), 42.2 (CH_2), 31.6 (CH_2), 29.4, 28.7, 25.9, 23.9, 9.6; ^{11}B NMR (96 MHz, C_6D_6): δ = –6.1 (br s); ^{19}F NMR (283 MHz, C_6D_6) δ = –76.2.

Preparation of 1.4a: A Schlenk flask was loaded with **1.3** (4.9 g, 10.3 mmol), benzimidazolylidene $\mathbf{L_a}$ (2.2 g, 10.1 mmol) and 100 mL of benzene. The reaction was stirred at 80 °C overnight and a suspension formed. The mixture was cooled to room temperature, and hexanes (60 mL) were added to further induce precipitation. The solid residue obtained by filtration was washed with hexanes (40 mL), and dried under vacuum to give **1.4a** (6.7 g, 95% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83 (m, 2H), 7.47 (m, 3H), 7.35 (d, *J* = 8 Hz, 2H), 4.98 (sept, *J* = 6.5 Hz, 2H), 2.72 (sept, *J* = 6.6 Hz, 2H), 2.21 (s, 2H), 1.90 (br s, 2H, BH_2), 1.62 (m, 16H), 1.45 (s, 6H), 1.39 (d, *J* = 6.6 Hz, 6H), 1.37 (d, *J* = 6.5 Hz, 6H), 1.10 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ =144.3

(C_q), 132.1 (C_q), 131.7 (C_q), 130.4 (CH_{Ar}), 126.0 (CH_{Ar}), 125.2 (CH_{Ar}), 114.8 (CH_{Ar}), 80.4 (C_q), 61.6 (C_q), 52.4, 40.4 (CH_2), 31.0 (CH_2), 29.9, 29.6, 26.6, 24.8, 20.9 10.0; ^{11}B NMR (96 MHz, $CDCl_3$): δ = –28.6 (t, J_{BH} = 82.9 Hz); ^{19}F NMR (283 MHz, CDCl3) δ = –78.0.

Preparation of 1.4b: A Schlenk flask was loaded with **1.3** (2.6 g, 5.5 mmol), cyclopropenylidene $\mathbf{L_b}$ (1.1 g, 4.7 mmol) and 80 mL of benzene. The reaction was stirred at 80 °C overnight and s suspension was formed. The mixture was cooled to room temperature, and hexanes (40 mL) were added to further induce precipitation. The solid obtained by filtration was washed with hexanes (40 mL). The resulting off white solid was dried under vacuum to give **1.4b** (2.7 g, 80% yield). ^{1}H NMR (300 MHz, CD_3CN): δ = 7.45 (t, J = 8 Hz, 1H), 7.45 (m, 2H), 4.00 (br s, 4H), 2.71 (sept, J = 6.5 Hz, 2H), 2.13 (s, 2H), 1.74 (br s, 2H, BH_2), 1.68 (m, 2H), 1.60 (m, 2H), 1.36 (s, 6H), 1.32 (m, 36H), 1.03 (t, J = 7.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 144.4 (C_q), 141.4 (C_q), 132.5 (C_q), 130.0 (CH_{Ar}), 125.6 (CH_{Ar}), 79.5 (C_q), 61.3 (C_q), 40.6 (CH_2), 30.8 (CH_2), 29.9, 29.5, 26.6, 24.5, 21.8, 10.0; ^{11}B NMR (96 MHz, $CDCl_3$): δ = –27.7 (t, J_{BH} = 87.9 Hz); ^{19}F NMR (283 MHz, CDCl3) δ = –79.3.

Preparation of 1.5a: **1.4a** (3.0 g, 4.3 mmol) was dissolved in 40 mL of CH_2Cl_2. An excess of triflic acid was added (2–5 eqs.). The solution was stirred and the reaction was monitored by ^{11}B NMR spectroscopy. Upon completion, the mixture was opened to air and cooled in an ice bath. Excess triethylamine (6 eq.) was added to neutralize the excess of triflic acid. The mixture was washed with water (4 x 50 mL). The organic phase was collected, dried with $MgSO_4$, filtered, and the volatiles were removed, giving an oily residue. 60 mL of ether was added and the emulsion stirred vigorously for several hours, which induced the formation of a powder. After filtration, the solid was dried under vacuum, and **1.5a** was obtained as a white solid (2.6 g, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.0 (m, 2H), 7.9 (m, 2H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.62 (m, 4H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.0 Hz, 1H), 7.50 (m, 4H), 7.35 (m, 3H), 7.17 (d, *J* = 7.8 Hz, 1H), 5.48 (sept, *J* = 7.0 Hz, 2H), 5.06 (sept, *J* = 7.0 Hz, 1H), 4.59 (sept, *J* = 6.7 Hz, 2H), 4.01 (sept, *J* = 6.7 Hz, 1H), 2.84 (sept, *J* = 6.5 Hz, 2H), 2.71 (sept, *J* = 6.5 Hz, 1H), 2.59 (sept, *J* = 6.5 Hz, 2H), 2.46-2.36 (m, 6H), 2.21 (m, 4H), 2.12 (m, 1H), 1.94 (d, *J* = 6.8 Hz, 6H), 1.91 (d, *J* = 7.0 Hz, 6H), 1.83 (d, *J* = 7.0 Hz, 6H), 1.77 (d, *J* = 6.8 Hz, 6H), 1.73 (s, 6H) 1.71 (d, *J* = 3.0 Hz, 6H), 1.70 (d, *J* = 2.7 Hz, 6H), 1.67 (s, 3H), 1.54 (d, *J* = 6.5 Hz, 6H), 1.43 (m, 16H), 1.37 (m, 18H), 1.30 (s, 6H), 1.25 (s, 3H), 1.21 (d, *J* = 6.5 Hz, 6H), 1.17 (m, 8H), 1.00 (t, *J* = 7.3 Hz, 6H), 0.88 (d, *J* = 7.0 Hz, 6H), –0.26 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.2, 144.2, 144.1, 143.1, 132.5, 132.4, 131.9, 131.6, 131.2, 131.1, 130.9, 127.6, 127.3, 126.8, 126.6, 126.5, 126.2, 122.3, 119.8, 118.9, 116.2, 115.9, 115.8, 115.3, 83.9, 83.2, 64.5, 61.4, 53.6, 53.1, 52.7, 52.6, 46.3, 42.2, 40.5, 32.2, 32.0, 31.6, 31.5, 30.3, 30.0, 29.9, 29.4, 29.2, 27.4, 27.3, 26.5, 26.3, 25.8, 25.6, 25.4, 25.3, 24.7, 22.5, 22.2, 22.1, 21.3, 21.2, 21.1, 20.8, 20.7, 11.0, 10.7, 10.0, 9.6, 8.9; ^{11}B NMR (96 MHz, $CDCl_3$): δ = –7.5 (br s); ^{19}F NMR (283 MHz, $CDCl_3$) δ = –75.4, –78.1. **1.5a** and $NaBPh_4$ were stirred for two hours at room temperature in CH_2Cl_2. After filtration, the solution was evaporated to give the corresponding BPh_4 salt, which was crystallized by slow diffusion of pentane in a saturated CH_2Cl_2 solution.

Preparation of 1.5b: **1.4b** (2.0 g, 2.8 mmol) was dissolved in 30 mL of CH_2Cl_2, and an excess of triflic acid was added (2–5 eqs.). The solution was stirred and the reaction was monitored by ^{11}B NMR spectroscopy. Upon completion, the mixture was opened to air and cooled in an ice bath. Excess triethylamine (6 eq.) was added to neutralize the excess of triflic acid. The mixture was washed with water (4 x 50 mL). The organic phase was collected, dried with $MgSO_4$, filtered, and the volatiles were removed, giving an oily residue. 60 mL of ether was added and the emulsion stirred vigorously for several hours, which induced the formation of a powder. After filtration, the solid was dried under vacuum, and **1.5b** was obtained as an off white solid (1.6 g, 67% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 (t, *J* = 7.8 Hz, 1H), 7.29 (m, 2H), 4.19 (br, 1H), 4.04 (sept, *J* = 6.5 Hz, 2H), 3.80 (br, 1H, B*H*), 2.66 (sept, *J* = 6.5 Hz, 1H), 2.52 (sept, *J* = 6.5 Hz, 1H), 2.24 (m, 2H), 1.93 (m, 1H), 1.71 (m, 2H), 1.45-1.21 (m, 43H), 1.08 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 143.9 (C_q), 143.8 (C_q), 141.0 (C_q), 140.5 (C_q), 131.7 (C_q), 130.8 (CH_{Ar}), 126.2 (CH_{Ar}), 126.1 (CH_{Ar}), 82.9 (C_q), 62.1 (C_q), 52.3, 41.0 (CH_2), 31.8 (CH_2), 29.9 (CH_2), 29.5, 29.1, 25.6, 25.4, 25.3, 25.2, 22.7, 22.2, 22.1, 22.0, 21.7, 21.0, 10.0, 9.7; ^{11}B NMR (96 MHz, $CDCl_3$): δ= –5.1 (br s); ^{19}F NMR (283 MHz, $CDCl_3$) δ = –76.2, –78.0. **1.5b** and $NaBPh_4$ were stirred for two hours at room temperature in CH_2Cl_2. After filtration, the solution was evaporated to give the corresponding BPh_4 salt, which was crystallized by slow diffusion of pentane in a saturated CH_2Cl_2 solution.

Preparation of 1.6a: **1.5a** (2.0 g, 2.4 mmol) and KC_8 (800 mg, 5.9 mmol) were loaded into a Schlenk flask. 20 mL of THF was added which induced an immediate deep blue color. The mixture was stirred for three hours. The volatiles were removed, and the residue was extracted with 40 mL of pentane. The solution was evaporated to dryness, which gave **1.6a** as a blue solid (1.1 g, 87% yield). Single crystals were obtained by slow evaporation of a saturated pentane solution. M.p.: 112 ^{o}C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 6.99 (br s, 3H), 6.94 (m, 2H), 6.71 (m, 2H), 5.47 (sept, *J* = 6.7 Hz, 2H), 3.63

(sept, *J* = 6.5 Hz, 2H), 2.51 (s, 1H, B*H*), 1.86 (s, 2H), 1.51 (m, 2H), 1.49 (m, 2H), 1.40 (d, *J* = 6.6 Hz, 6H), 1.35 (d, *J* = 6.6 Hz, 6H), 1.20 (s, 6H), 1.07 (d, *J* = 7.0, 12H), 0.97 (t, *J* = 7.4, 6H); ^{13}C NMR (75 MHz, C_6D_6): δ = 151.4 (C_q), 140.0 (C_q), 133.1 (C_q), 126.6 (CH_{Ar}), 124.3 (CH_{Ar}), 122.2 (CH_{Ar}), 112.7 (CH_{Ar}), 63.7 (C_q), 52.1 (C_q), 51.2, 47.3 (CH_2), 35.6 (CH_2), 31.0, 28.8, 28.0, 24.4, 20.5, 10.7; ^{11}B NMR (96 MHz, $CDCl_3$): δ = –1.3 (d, J_{BH} = 82.4 Hz).

Preparation of 1.6b: **1.5b** (1.5 g, 1.7 mmol) and KC_8 (600 mg, 4.4 mmol) were loaded into a Schlenk flask. 20 mL of THF was added which induced an immediate deep red color. The mixture was stirred for three hours. The volatiles were evaporated, and the residue was extracted with 40 mL of pentane. The solution was evaporated to dryness, which gave **1.6b** as a red solid (0.8 g, 82% yield). Single crystals were obtained by slow evaporation of a saturated pentane solution. M.p.: 135 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 7.16 (br, 1H), 7.00 (br, 2H), 3.59-3.38 (m, 6H), 2.73 (s, 1H, B*H*), 1.98 (q, *J* = 7.4 Hz, 4H), 1.91 (s, 2H), 1.49 (d, *J* = 6.6 Hz, 6H), 1.30 (d, *J* = 6.8 Hz, 6H), 1.22 (s, 6H), 1.09 (t, *J* = 7.4 Hz, 6H), 0.86 (d, *J* = 6.8 Hz, 24H); ^{13}C NMR (75 MHz, C_6D_6): δ = 150.7 (C_q), 140.0 (C_q), 135.1 (C_q), 126.7 (CH_{Ar}), 124.2 (CH_{Ar}), 64.7 (C_q), 52.2 (C_q), 50.0, 48.3 (CH_2), 34.9 (CH_2), 30.8, 29.0, 27.9, 24.5, 22.3, 10.5; ^{11}B NMR (96 MHz, C_6D_6): δ = 0.8 (d, J_{BH} = 89.7 Hz).

Protonation of 1.6a,b: HOTf (1.2 eq) was added at room temperature to a benzene solution (5 mL) of **1.6a,b** (100 mg, 0.19 mmol; 100 mg, 0.18 mmol). The solution immediately turned colorless. After stirring for 30 minutes, the volatiles were removed under vacuum, and the residue was extracted with 10 mL of dichloromethane. The solvent was removed and the residue was washed with hexanes. ^{1}H, ^{13}C, ^{11}B, and ^{19}F

NMR spectra were identical to those of **1.4a,b**. **1.4a:** 110 mg, 86% yield; **1.4b**: 107 mg, 85% yield. Further TfOH addition led to compounds **1.5a,b** as described above.

Observation of 1.7b: **1.5b** (100 mg, 0.116 mmol) was dissolved in 5 mL of DME. To the stirred solution, one equivalent of KC_8 was added. The colorless solution became red immediately. An aliquot was taken and checked by NMR and EPR. The ^{1}H, ^{13}C and ^{11}B NMR spectra were silent, but one fluorine signal corresponding to a free triflate group was observed (–78.1 ppm).

Preparation of 1.11: Compound **1.10** (3.5 g, 10.3 mmol) was dissolved in 70 mL of benzene then trifluoromethanesulfonic acid (2.0 mL, 22.7 mmol) was added slowly, causing an immediate precipitation and vigorous bubbling of H_2 gas. The mixture was stirred overnight and then cannula filtered. The solid was washed with benzene (2 X 40 mL) and dried under vacuum affording 5.3 g (8.3 mmol, 80% yield) of **1.11** as a white solid. Colorless single crystals were obtained by vapor diffusion of pentane in a saturated chloroform solution. M.p.: 235 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (t, *J* = 8 Hz, 1H), 7.31 (d, *J* = 8 Hz, 2H), 3.46 (s, 1H, B*H*) 2.55 (sept, *J* = 6.5 Hz, 2H), 2.38 (m, 2H), 2.27 (s, 2H), 1.79 (m, 6H) 1.41, (br s, 2H), 1.37 (s, 6H), 1.32 (d, *J* = 6.5 Hz, 6H), 1.23 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.7 (C_q), 130.8 (CH_{Ar}), 130.5 (C_q), 125.6 (CH_{Ar}), 82.0 (C_q), 59.3 (C_q), 44.9 (CH_2), 34.6 (CH_2), 29.6, 29.3. 27.4, 25.0 (CH_2), 24.1, 22.0 (CH_2); ^{11}B NMR (160 MHz, $CDCl_3$): δ = –2.2 (br s); ^{19}F NMR (472 MHz, $CDCl_3$) δ = –76.2. HRMS: m/z calculated for $C_{25}H_{36}BF_6NNaO_6S_2$ $(M+Na)^+$ 653.2324, found 653.2329.

Preparation of 1.12: Compound **1.11** (5.0 g, 7.8 mmol) was dissolved in 80 mL of THF. NaCN (0.81 g, 16.5 mmol) was added under a flow of argon. The mixture was stirred for three days, monitored by ^{19}F and ^{11}B NMR, before evaporating the solvent under vacuum. The residue was extracted with 80 mL of dichloromethane and the solvent was removed under vacuum. The solid was washed with hexanes (3 X 20 mL) and dried to afford 2.6 g (6.7 mmol, 87% yield) of **1.12** as an off white powder. Colorless single crystals were obtained by vapor diffusion of hexanes in a saturated chloroform solution**.** M.p.: 282 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.47$ (t, $J = 8$ Hz, 1H), 7.30 (d, $J = 8$ Hz, 2H), 2.60 (m, 2H), 2.53 (sept, $J = 6.5$ Hz, 2H), 2.26 (s, 2H), 1.92 (m, 2H), 1.80 (m, 4H), 1.43 (m, 2H), 1.39 (s, 6H), 1.31 (d, $J = 6.5$ Hz, 6H), 1.21 (d, $J = 6.5$, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 144.5$ (C_q), 131.6 (C_q), 130.6 (CH_{Ar}), 125.2 (CH_{Ar}), 80.5 (C_q), 59.6 (C_q), 44.8 (CH_2), 35.8 (CH_2), 29.32, 29.31, 26.4, 24.7 (CH_2), 23.6, 22.0 (CH_2); ^{11}B NMR (160 MHz, $CDCl_3$): $\delta = -34.6$ (d, $J_{BH} = 94$ Hz). HRMS: m/z calculated for $C_{25}H_{37}BN_3$ $(M+H)^+$ 390.3080, found 390.3064.

Preparation of 1.13: **1.12** (366 mg, 0.94 mmol) and potassium bis(trimethylsilyl)amide (200 mg, 1.00 mmol) were loaded in a Schlenk flask under argon. THF (15 mL) was added to the solids and the mixture was stirred for 45 minutes. The volatiles were evaporated under vacuum and the residue was washed with 15 mL of ether then dried, affording 382 mg (0.89 mmol, 95% yield) of **1.13** as a yellow solid. Single yellow crystals were obtained by slow evaporation of a saturated THF solution. M.p.: 345 ºC. ^{1}H NMR (500 MHz, THF–d_8): $\delta = 7.06$ (d, $J = 7.5$ Hz, 1H), 6.96 (d, $J = 7.5$ Hz), 3.17 (sept, $J = 6.5$ Hz, 2H), 2.35 (m, 2H), 1.91 (s, 2H), 1.58 (m, 5H), 1.26 (d, $J = 6.5$ Hz, 6H), 1.13 (d, $J = 6.5$ Hz, 6H), 1.07 (s, 6H); ^{13}C NMR (125 MHz, THF–d_8): $\delta = 151.5$ (C_q), 139.4 (C_q), 127.0 (CH_{Ar}), 124.2 (CH_{Ar}), 64.9 (C_q), 51.9 (CH_2), 49.7 (C_q), 40.4 (CH_2), 30.3, 28.7, 26.6 (CH_2), 26.2, 25.2, 25.1 (CH_2); ^{11}B NMR (160 MHz, THF–d_8): $\delta = -17.9$.

HRMS: m/z calculated for $C_{25}H_{35}BN_3$ $(M)^-$ 388.2930, found 388.2992. An excess of dibenzo-18-crown-6 was added to the THF solution of **1.13**. Single crystals of **1.14** were obtained by slow evaporation. The ^{11}B NMR spectrum is identical to that of **1.13**.

Protonation of 1.13: Compound **1.13** (100 mg, 0.23 mmol) was dissolved in 5 mL of THF. A 2.0 M solution of HCl in ether (0.12 mL, 0.23 mmol) was added which immediately turns the yellow solution colorless. After stirring for 5 minutes, the volatiles were evaporated under vacuum. The residue was extracted with 10 mL of dichloromethane. The volatiles were removed under vacuum resulting in 82 mg (90% yield) of a white solid. ^{1}H, ^{13}C, and ^{11}B are identical to **1.12**.

Preparation of 1.15: **1.13** (100 mg, 0.23 mmol) was loaded in a Schlenk flask under argon and dissolved in 5 mL of THF. Isopropyl iodide (80 mg, 0.46 mmol) was added and the mixture was stirred overnight. Potassium iodide precipitated out of the reaction. The solvent was evaporated and the residue was extracted with 10 mL of dichloromethane. The solvent was reduced to create a saturated solution. Hexanes were added and the suspension was stored overnight at −20 ºC. After filtration 76 mg (0.18 mmol, 75% yield) of a white powder are collected. Colorless single crystals were obtained by vapor diffusion of hexanes in a saturated chloroform solution. M.p.: 294 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (t, *J* = 8 Hz, 1H), 7.31 (d, *J* = 8 Hz, 2H), 2.62 (sept, *J* = 6.5 Hz, 2H), 2.36 (m, 2H), 2.27 (br s, 2H), 1.87 (m, 4H), 1.78 (m, 1H) 1.62 (sept, *J* = 7 Hz, 1H), 1.44 (d, *J* = 6.5 Hz, 6H), 1.42 (br, 3H), 1.39 (s, 6H), 1.33 (d, *J* = 6.5 Hz, 6H), 1.01 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ =145.4, 131.7, 131.0, 125.7, 80.9, 60.7, 45.6, 35.8, 30.16, 29.3, 27.7, 25.2, 24.9, 22.3, 22.2; ^{11}B NMR (160

MHz, $CDCl_3$): δ = –21.9. HRMS: m/z calculated for $C_{28}H_{42}BN_3Na$ $(M+Na)^+$ 453.3400, found 453.3401.

Preparation of 1.16: **1.13** (100 mg, 0.23 mmol) and (trimethylphosphine)gold chloride (73 mg, 0.24 mmol) were loaded in a Schlenk flask and 10 mL of THF was added. The mixture was stirred for 2 hours and a precipitate appeared. The solvent was removed under vacuum and the residue was extracted with 10 mL dichloromethane. The solvent was removed and the solid was washed with 15 mL of ether to afford 107 mg (0.16 mmol, 69% yield) of an off white solid. Single crystals were grown from a saturated chloroform/ether (2:1 v/v) solution. M.p.: 160 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (t, J = 8 Hz, 1H), 7.23 (d, J = 8 Hz, 2H), 3.12 (m, 1H), 2.81 (m, 1H), 2.73 (m, 1H) 2.63 (m, 1H), 2.27 (m, 2H), 1.80 (br, 2H), 1.69 (br, 1H) 1.63 (br, 2H), 1.53 (br d, 3H), 1.46 (d, J = 9.5 Hz, 9H), 1.42 (br, 6H), 1.31 (br, 3H), 1.29 (br, 3H), 1.24 (br, 3H), 1.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.0, 147.2, 133.61, 133.60, 129.8, 125.0, 72.5, 54.6, 47.7, 40.8, 36.9, 32.6, 30.1, 29.4, 28.6, 28.4, 27.2, 25.9, 25.6, 24.9, 24.3, 24.1, 23.0, 16.5, 16.3; ^{11}B NMR (160 MHz, $CDCl_3$): δ = –26.2 (d, J_{BP} = 30 Hz); ^{31}P NMR (202 MHz, $CDCl_3$): δ = 10.1 (br m). HRMS: m/z calculated for $C_{28}H_{45}AuBN_3P$ $(M+H)^+$ 662.3109, found 662.3110.

3) Crystallographic Data

Compound	**1.3**
Empirical formula	$C_{23}H_{37}BF_3NO_3S$
Formula weight	475.41
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.1389(6)
b/Å	13.5546(7)
c/Å	16.2662(9)

α/°	90.00
β/°	95.4560(10)
γ/°	90.00
Volume/Å^3	2444.8(2)
Z	4
ρ_{calc}mg/mm^3	1.292
m/mm^{-1}	0.180
F(000)	1016.0
Crystal size/mm^3	0.32 × 0.17 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	4.26 to 58.72°
Index ranges	$-15 \le h \le 14$, $-18 \le k \le 13$, $-21 \le l \le 22$
Reflections collected	19841
Independent reflections	6162 [R_{int} = 0.0132, R_{sigma} = 0.0121]
Data/restraints/parameters	6162/0/401
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0326, wR_2 = 0.0872
Final R indexes [all data]	R_1 = 0.0346, wR_2 = 0.0889
Largest diff. peak/hole / e Å^{-3}	0.44/-0.32

Compound	**1.5a(BPh$_4$)**
Empirical formula	$C_{60}H_{74}B_2F_3N_3O_3S$
Formula weight	995.90
Temperature/K	100
Crystal system	monoclinic
Space group	P2$_1$/c
a/Å	14.2524(5)
b/Å	13.4771(5)
c/Å	28.1965(9)
α/°	90
β/°	91.7220(10)
γ/°	90
Volume/Å^3	5413.6(3)
Z	4
ρ_{calc}mg/mm^3	1.222
m/mm^{-1}	0.118
F(000)	2128.0
Crystal size/mm^3	0.25 × 0.22 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	5.018 to 52.78°
Index ranges	$-17 \le h \le 17$, $-16 \le k \le 16$, $-33 \le l \le 34$
Reflections collected	34655
Independent reflections	10835 [R_{int} = 0.0671, R_{sigma} = 0.0686]
Data/restraints/parameters	10835/0/661

Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	$R_1 = 0.0479$, $wR_2 = 0.1248$
Final R indexes [all data]	$R_1 = 0.0620$, $wR_2 = 0.1350$
Largest diff. peak/hole / e Å^{-3}	0.56/-0.49

Compound	**1.5b(BPh$_4$)**
Empirical formula	$C_{62}H_{84}B_2F_3N_3O_3S$
Formula weight	1030.00
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	22.260(12)
b/Å	13.788(7)
c/Å	19.769(10)
α/°	90.00
β/°	106.570(7)
γ/°	90.00
Volume/Å^3	5816(5)
Z	4
ρ_{calc}mg/mm^3	1.176
m/mm^{-1}	0.112
F(000)	2216.0
Crystal size/mm^3	0.28 × 0.14 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	4.82 to 46.56°
Index ranges	$-24 \le h \le 24$, $-15 \le k \le 13$, $-21 \le l \le 20$
Reflections collected	24181
Independent reflections	8342 [$R_{int} = 0.1417$, $R_{sigma} = 0.2426$]
Data/restraints/parameters	8342/79/763
Goodness-of-fit on F^2	0.787
Final R indexes [I>=2σ (I)]	$R_1 = 0.0522$, $wR_2 = 0.0744$
Final R indexes [all data]	$R_1 = 0.1833$, $wR_2 = 0.0995$
Largest diff. peak/hole / e Å^{-3}	0.35/-0.30

Compound	**1.6a**
Empirical formula	$C_{35}H_{54}BN_3$
Formula weight	527.62
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	16.2182(7)
b/Å	9.3515(4)
c/Å	21.6436(10)

α/°	90
β/°	104.492(2)
γ/°	90
Volume/Å^3	3178.1(2)
Z	4
ρ_{calc}mg/mm^3	1.103
m/mm^{-1}	0.063
F(000)	1160.0
Crystal size/mm^3	0.2 × 0.18 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	2.826 to 52.794°
Index ranges	$-19 \leq h \leq 20$, $-11 \leq k \leq 11$, $-24 \leq l \leq 27$
Reflections collected	22614
Independent reflections	6500 [R_{int} = 0.0372, R_{sigma} = 0.0422]
Data/restraints/parameters	6500/0/359
Goodness-of-fit on F^2	1.111
Final R indexes [I>=2σ (I)]	R_1 = 0.0492, wR_2 = 0.1318
Final R indexes [all data]	R_1 = 0.0786, wR_2 = 0.1654
Largest diff. peak/hole / e Å^{-3}	0.39/-0.58

Compound	**1.6b**
Empirical formula	$C_{39.5}H_{70}BN_3$
Formula weight	597.80
Temperature/K	100
Crystal system	monoclinic
Space group	C2/c
a/Å	27.415(5)
b/Å	18.243(4)
c/Å	17.305(3)
α/°	90.00
β/°	114.471(2)
γ/°	90.00
Volume/Å^3	7877(3)
Z	8
ρ_{calc}mg/mm^3	1.008
m/mm^{-1}	0.057
F(000)	2664.0
Crystal size/mm^3	0.20 × 0.18 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	4.22 to 68.72°
Index ranges	$-43 \leq h \leq 39$, $-28 \leq k \leq 28$, $-19 \leq l \leq 27$
Reflections collected	32951
Independent reflections	15374 [R_{int} = 0.0609, R_{sigma} = 0.0878]
Data/restraints/parameters	15374/0/587

Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	$R_1 = 0.0629$, $wR_2 = 0.1547$
Final R indexes [all data]	$R_1 = 0.1173$, $wR_2 = 0.1813$
Largest diff. peak/hole / e Å^{-3}	0.93/-0.46

Compound	**1.11**
Empirical formula	C25H36BF6NO6S2
Formula weight	635.48
Temperature/K	100(2)
Space group	P21/c
a/Å	9.4957(2)
b/Å	15.8660(4)
c/Å	21.1934(5)
α/°	90.00
β/°	112.3930(10)
γ/°	90.00
Volume/Å^3	2952.20(12)
Z	4
ρcalcg/cm^3	1.430
μ/mm^{-1}	0.258
F(000)	1328.0
Crystal size/mm^3	0.27 × 0.21 × 0.19
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.3 to 50.8
Index ranges	$-11 \le h \le 11$, $-17 \le k \le 19$, $-25 \le l \le 25$
Reflections collected	17832
Independent reflections	5426 [Rint = 0.0180]
Data/restraints/parameters	5426/0/376
Goodness-of-fit on F^2	1.089
Final R indexes [I>=2σ (I)]	R1 = 0.0313, wR2 = 0.0761
Final R indexes [all data]	R1 = 0.0387, wR2 = 0.0861
Largest diff. peak/hole / e Å^{-3}	0.37/-0.37

Compound	**1.12**
Empirical formula	$C_{25}H_{36}BN_3$
Formula weight	389.38
Temperature/K	100(2)
Space group	$Pca2_1$
a/Å	20.423(2)
b/Å	11.7432(13)
c/Å	9.5819(11)
α/°	90.00
β/°	90.00
γ/°	90.00

Volume/Å^3	2298.0(4)
Z	4
ρ_{calc}g/cm^3	1.125
μ/mm^{-1}	0.065
F(000)	848.0
Crystal size/mm^3	0.12 × 0.07 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.98 to 50.76
Index ranges	$-24 \leq h \leq 22$, $-8 \leq k \leq 14$, $-11 \leq l \leq 11$
Reflections collected	8494
Independent reflections	4005 [R_{int} = 0.0739]
Data/restraints/parameters	4005/1/268
Goodness-of-fit on F^2	0.950
Final R indexes [I>=2σ (I)]	R_1 = 0.0613, wR_2 = 0.1218
Final R indexes [all data]	R_1 = 0.1080, wR_2 = 0.1383
Largest diff. peak/hole / e Å^{-3}	0.24/-0.28

Compound	**1.13**
Empirical formula	$C_{103}H_{144.54}B_4K_4N_{12}O_{0.75}$
Formula weight	1762.49
Temperature/K	200(2)
Space group	C2/c
a/Å	40.3726(10)
b/Å	22.7967(6)
c/Å	30.3555(9)
α/°	90.00
β/°	128.5740(10)
γ/°	90.00
Volume/Å^3	21842.0(10)
Z	8
ρ_{calc}g/cm^3	1.072
μ/mm^{-1}	1.810
F(000)	7588.0
Crystal size/mm^3	0.14 × 0.08 × 0.04
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.78 to 129.32
Index ranges	$-32 \leq h \leq 45$, $-24 \leq k \leq 25$, $-34 \leq l \leq 31$
Reflections collected	55901
Independent reflections	16647 [R_{int} = 0.0577]
Data/restraints/parameters	16647/0/1258
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0690, wR_2 = 0.2091
Final R indexes [all data]	R_1 = 0.1034, wR_2 = 0.2413
Largest diff. peak/hole / e Å^{-3}	1.97/-0.48

Compound	**1.14**
Empirical formula	$C_{45}H_{59}BKN_3O_6$
Formula weight	787.86
Temperature/K	100(2)
Space group	$P2_1/c$
a/Å	13.4520(2)
b/Å	33.9488(6)
c/Å	9.1362(2)
α/°	90.00
β/°	90.7390(10)
γ/°	90.00
Volume/Å^3	4171.97(13)
Z	4
ρ_{calc}g/cm^3	1.254
μ/mm^{-1}	1.521
F(000)	1688.0
Crystal size/mm^3	0.2 × 0.2 × 0.15
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.2 to 135.94
Index ranges	$-14 \leq h \leq 15$, $-39 \leq k \leq 40$, $-10 \leq l \leq 10$
Reflections collected	26753
Independent reflections	7231 [R_{int} = 0.0284]
Data/restraints/parameters	7231/0/535
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0385, wR_2 = 0.1011
Final R indexes [all data]	R_1 = 0.0424, wR_2 = 0.1045
Largest diff. peak/hole / e Å^{-3}	0.36/-0.20

Compound	**1.15**
Empirical formula	$C_{29}H_{43}BCl_3N_3$
Formula weight	550.82
Temperature/K	100(2)
Space group	Pbca
a/Å	18.6085(9)
b/Å	8.7906(4)
c/Å	35.9538(16)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	5881.3(5)
Z	8
ρ_{calc}g/cm^3	1.244
μ/mm^{-1}	0.335
F(000)	2352.0
Crystal size/mm^3	0.2 × 0.2 × 0.15

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.04 to 50.06
Index ranges	$-22 \le h \le 22$, $-10 \le k \le 10$, $-42 \le l \le 42$
Reflections collected	35318
Independent reflections	5203 [R_{int} = 0.0637]
Data/restraints/parameters	5203/0/333
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0448, wR_2 = 0.1057
Final R indexes [all data]	R_1 = 0.0525, wR_2 = 0.1098
Largest diff. peak/hole / e Å^{-3}	0.38/-0.41

Compound	**1.16**
Empirical formula	$C_{28}H_{44}AuBN_3P$
Formula weight	661.41
Temperature/K	100(2)
Space group	$P2_1/c$
a/Å	10.0672(9)
b/Å	21.840(2)
c/Å	15.3642(11)
α/°	90.00
β/°	120.922(5)
γ/°	90.00
Volume/Å^3	2898.0(4)
Z	4
ρ_{calc}g/cm^3	1.516
μ/mm^{-1}	5.152
F(000)	1328.0
Crystal size/mm^3	0.2 × 0.2 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.52 to 50.78
Index ranges	$-12 \le h \le 12$, $-26 \le k \le 23$, $-18 \le l \le 17$
Reflections collected	19149
Independent reflections	5278 [R_{int} = 0.0278]
Data/restraints/parameters	5278/0/316
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0285, wR_2 = 0.0670
Final R indexes [all data]	R_1 = 0.0364, wR_2 = 0.0695
Largest diff. peak/hole / e Å^{-3}	1.72/-1.07

4) Computational Details

Calculations were performed with the Gaussian 09 program package[26] using the BVP86/6- 311+g(2d,p) and (U)BVP86/6-311+g(2d,p) level of theory.[27] All energies were corrected for (unscaled) zero-point vibrational energy contributions with this method.

The structures represented here correspond to energetic minima indicated by the absence of negative frequencies. The Cartesian coordinates and the sum of electronic and zero-point energies are as follows:

1.6a

ZPE = -1555.016793 a.u.

7	-2.760659	-0.857173	-0.265591
7	-2.580762	1.353835	-0.179798
6	-6.431988	-0.107274	-0.614238
1	-7.417805	-0.560432	-0.731193
6	-5.306048	-0.936664	-0.525217
1	-5.421102	-2.017437	-0.566294
6	-4.052987	-0.332354	-0.377258
6	-1.827142	0.180578	-0.154761
6	0.737070	-0.471513	0.696495
6	2.700331	0.346806	-0.646261
6	3.109515	1.708896	-0.580058
6	2.737818	2.643597	0.569805
1	2.228910	2.039839	1.335354
6	1.736394	3.711162	0.077114
1	2.216539	4.406133	-0.630019
1	1.357756	4.304707	0.924503
1	0.886042	3.244597	-0.436134
6	-6.312163	1.286928	-0.555191
1	-7.205726	1.909634	-0.624704
6	-2.373278	-2.199003	-0.767137
1	-1.290994	-2.234018	-0.582590
6	-2.601163	-2.291612	-2.283309
1	-3.665712	-2.194611	-2.540941
1	-2.249093	-3.265787	-2.653377
1	-2.040983	-1.503865	-2.805553
6	-3.049732	-3.350627	-0.011988
1	-3.043844	-3.190006	1.074317
1	-2.507541	-4.283828	-0.222094
1	-4.090068	-3.504755	-0.329145
6	-1.993030	2.683880	0.066198
1	-0.931651	2.455643	0.243548
6	-2.093856	3.577711	-1.174720
1	-1.627167	3.087977	-2.040822
1	-1.568126	4.526379	-0.992520
1	-3.135863	3.815114	-1.434652
6	-2.553503	3.329942	1.340700
1	-3.619779	3.580723	1.259057
1	-2.004637	4.260442	1.546614
1	-2.423498	2.660175	2.202504
6	-3.933879	1.074633	-0.323305
6	-5.061390	1.899994	-0.413189
1	-4.981084	2.985309	-0.384809
6	0.542209	-1.163138	2.065742
6	1.982120	-1.342697	2.628223
1	2.121823	-0.699822	3.509922
1	2.169221	-2.373820	2.962450
6	3.759728	-2.143896	0.962400
1	3.080182	-2.900739	0.552348
1	4.361238	-2.615093	1.755489
1	4.449292	-1.826876	0.166561
6	2.901760	-0.387395	-1.847837
6	3.597398	0.218379	-2.904964
1	3.764902	-0.348294	-3.823963
6	4.073114	1.523148	-2.812797
1	4.626093	1.969809	-3.642291
6	3.808352	2.261912	-1.663869
1	4.138302	3.301909	-1.608130
6	3.948886	3.350466	1.210877
1	4.708981	2.643052	1.566673
1	3.622735	3.961468	2.067373
1	4.436106	4.030251	0.494735
6	2.336648	-1.785570	-2.079794
1	1.897440	-2.124199	-1.131728
6	1.198410	-1.729433	-3.119590
1	0.419389	-1.023419	-2.799989
1	0.741333	-2.724020	-3.244591
1	1.575993	-1.408230	-4.103266
6	3.400737	-2.809497	-2.521574
1	3.821578	-2.553808	-3.506290
1	2.950444	-3.810695	-2.610766
1	4.235405	-2.875390	-1.809921
6	4.049671	0.027805	2.118327
1	4.739845	0.386492	1.341441
1	4.645708	-0.505039	2.875336
1	3.580774	0.891983	2.605830
6	-0.211515	-2.515117	1.999081
1	-0.302035	-2.903026	3.027901
1	-1.239306	-2.306315	1.669427
6	0.400294	-3.613378	1.126764

1	0.539511	-3.277815	0.087551
1	-0.246428	-4.503937	1.112825
1	1.380678	-3.937135	1.506431
6	-0.268846	-0.199338	2.991913
1	0.251909	0.772894	2.988963
1	-1.245832	-0.016903	2.518192
6	-0.482857	-0.656711	4.443067
1	-1.136498	-1.538492	4.512327
1	-0.959795	0.145443	5.026820
1	0.464969	-0.904581	4.946336
5	-0.282899	0.182652	-0.177492
1	0.137025	1.025567	-0.941961
7	2.116572	-0.287318	0.510741
6	2.998402	-0.932590	1.538171

1.6b

ZPE = -1637.070368 a.u.

7	2.573481	-0.529452	-0.288128
7	-3.116079	2.168925	-0.099532
7	-3.294795	-1.591727	0.338662
5	0.159875	0.239096	-0.053507
6	-1.364320	0.169519	-0.087023
6	-2.644290	-0.427759	0.090209
6	-2.563973	0.943602	-0.028665
6	1.203408	-0.690494	-0.581087
6	1.129503	-1.757570	-1.689491
6	2.452724	-2.541227	-1.501529
6	3.477599	-1.573404	-0.873535
6	3.066453	0.426608	0.668173
6	3.622436	1.656015	0.220022
6	4.199158	2.524867	1.159456
6	4.201901	2.225130	2.518542
6	3.587743	1.055451	2.959158
6	3.005020	0.147956	2.062160
6	-0.070845	-2.715027	-1.560337
6	-0.143117	-3.813308	-2.632599
6	1.127203	-1.058764	-3.094714
6	-0.186009	-0.404300	-3.531418
6	4.316488	-2.292524	0.199668
6	4.466402	-1.014490	-1.918248
6	3.531759	2.124285	-1.229871
6	4.888206	2.552235	-1.821523
6	2.517398	3.280814	-1.353062
6	2.282137	-1.064929	2.643399
6	3.175320	-1.907500	3.576072
6	1.008198	-0.624151	3.395284
6	-2.254135	3.362007	-0.324546
6	-1.342254	3.642007	0.877788
6	-1.476426	3.250658	-1.640442
6	-4.572459	2.368484	0.058164
6	-5.214724	2.964472	-1.204733
6	-4.919573	3.180443	1.315249
6	-2.489300	-2.678808	0.959388
6	-2.753955	-4.044352	0.313914
6	-2.648431	-2.743477	2.487333
6	-4.770684	-1.701442	0.333373
6	-5.351215	-1.260854	-1.017392
6	-5.455849	-1.017792	1.531868
1	2.278372	-3.375464	-0.801755
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1	-0.996345	-4.483994	-2.448083
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1	-0.551341	0.280940	-2.752561
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1	4.934710	-3.067787	-0.279107
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1	5.069320	-1.840057	-2.327851
1	5.158074	-0.298391	-1.453542
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1	5.283950	3.445935	-1.314093
1	4.777379	2.805318	-2.887679
1	5.647190	1.761375	-1.738581
1	1.539541	2.981155	-0.954665
1	2.390988	3.570891	-2.408462
1	2.860484	4.168418	-0.797641
1	1.955867	-1.690362	1.799726
1	4.110577	-2.216747	3.088761

1	2.640310	-2.814937	3.898322
1	3.444896	-1.348903	4.485849
1	1.255205	0.024549	4.251233
1	0.471859	-1.504499	3.785391
1	0.335826	-0.075692	2.720869
1	-2.960866	4.201692	-0.415937
1	-1.928748	3.756667	1.800878
1	-0.777922	4.572482	0.713011
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1	-4.980947	1.358384	0.186665
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1	-6.308770	2.994398	-1.090263
1	-4.977242	2.360656	-2.092023
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1	-4.540924	4.211551	1.249166
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1	-1.914918	-3.449502	2.906220
1	-3.648515	-3.098315	2.781177
1	-4.967379	-2.780352	0.425027
1	-5.151734	-0.199932	-1.223681
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1	-4.912193	-1.847711	-1.836212
1	-5.119091	-1.450949	2.482317
1	-6.547476	-1.144998	1.467719
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1	0.562126	1.258127	0.466208

1.7b
ZPE = -1636.908744 a.u.

7	-2.554550	-0.425371	0.394967
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6	-1.134734	-1.332922	2.042986
6	-2.488206	-2.091008	2.069223
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6	-3.559200	1.629807	-0.578200
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6	-3.036743	-0.298688	-2.032947
6	0.040246	-2.335499	2.022259
6	0.127578	-3.239639	3.260317
6	-1.034817	-0.375264	3.280183
6	0.313916	0.305050	3.524613
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6	-4.428251	-0.417589	2.114120
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6	-4.786733	3.006947	1.199471
6	-2.412748	3.563435	0.561069
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6	-3.311498	-2.630091	-3.049964
6	-1.084840	-1.441130	-3.145538
6	2.358774	3.351009	0.012915
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6	1.514779	3.427642	1.287311
6	4.655124	2.221334	-0.080926
6	5.189849	2.816633	1.228174
6	5.138044	2.991484	-1.315921
6	2.347012	-2.862669	-0.676134
6	2.697805	-3.987586	0.303387
6	2.414223	-3.327039	-2.136618
6	4.668481	-1.782590	-0.657320
6	5.445312	-1.464310	0.625676
6	5.154207	-1.026426	-1.900028
1	-2.358865	-3.080706	1.603113
1	-2.856632	-2.256867	3.090329
1	-4.525985	3.279850	-1.573019
1	-4.618717	2.180068	-3.789337
1	-3.614166	-0.062297	-4.096595
1	-0.072514	-2.967977	1.126063
1	0.987058	-1.786526	1.902365
1	0.302630	-2.665840	4.181553
1	0.956314	-3.955393	3.159598
1	-0.790793	-3.827608	3.403617

1	-1.813260	0.396952	3.183337
1	-1.307345	-0.962682	4.172242
1	1.103275	-0.419244	3.773093
1	0.235808	1.004598	4.369718
1	0.646631	0.878670	2.648378
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1	-3.886539	0.238146	2.807062
1	-5.055724	-1.092474	2.714204
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1	-5.154888	3.780934	0.509742
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1	-2.283154	4.098175	1.514538
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1	-2.082321	-2.096030	-1.362982
1	-4.261229	-2.769842	-2.515884
1	-2.826481	-3.612998	-3.149747
1	-3.550837	-2.282387	-4.065734
1	-1.308696	-0.986714	-4.122465
1	-0.592618	-2.408128	-3.331683
1	-0.377564	-0.781021	-2.622163
1	3.111365	4.150480	0.060874
1	2.181002	3.541983	-2.157564
1	1.021010	4.518551	-1.228413
1	0.776857	2.764318	-1.378092
1	0.718223	2.670647	1.290757
1	1.034015	4.414208	1.349561
1	2.133256	3.291029	2.185241
1	5.023260	1.191011	-0.156720
1	4.869771	3.859369	1.369199
1	6.289177	2.813653	1.211675
1	4.858473	2.232334	2.098116
1	4.763858	2.539117	-2.245174
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1	1.323049	-2.522391	-0.470101
1	3.696145	-4.408146	0.110587
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1	2.132939	-2.521217	-2.828073
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1	3.416730	-3.690041	-2.408333
1	4.812039	-2.853430	-0.858322
1	5.290136	-0.430058	0.962585
1	6.522678	-1.604544	0.458108
1	5.137099	-2.131111	1.442780
1	4.642402	-1.386201	-2.802829
1	6.233728	-1.184317	-2.035759
1	4.980858	0.055078	-1.826787
1	-0.563007	1.146233	-0.749704

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Chapter 2:

Novel Carbene-Stabilized Group 15 Compounds

Introduction

In 2008, the discovery by Robinson and co-workers of silicon(0) compound **2.A**[1] (Figure 2.1) clearly demonstrated that carbenes could stabilize a main group element in its zero oxidation state.[2] Since then, the use of carbenes as entities to stabilize reactive fragments has experienced impressive growth.[3] As illustrated in the previous chapter, the choice of carbene can have a drastic impact on the ensuing product. The varying electronic and steric properties of the carbenes generate differing outcomes.[4] For example, the activation of white phosphorus has led to P_1,[5] P_4,[5] P_8,[6] and P_{12}[7] clusters (**2.B**–**2.F** respectively) among others,[8] with each featuring different carbenes (Figure 2.1). Even more apparent, the bis(NHC)–P_2 complex can undergo two sequential oxidations while the analogues bis(CAAC)–P_2 can only be oxidized once.[9] The P_2 fragment is significantly less electron rich because of the CAACs ability to accept much more electron density compared to the NHC. Recent studies have shown that the smaller HOMO–LUMO gap of CAACs compared to NHCs, make CAACs both more nucleophilic and also more electrophilic.[10] These properties create a considerable difference between these two carbenes. CAACs are able to activate small molecules like H_2, NH_3,[11] and CO[12] at room temperature, while NHCs cannot. Thus, electronics is a crucial property to consider when choosing the appropriate carbene for the desired task.

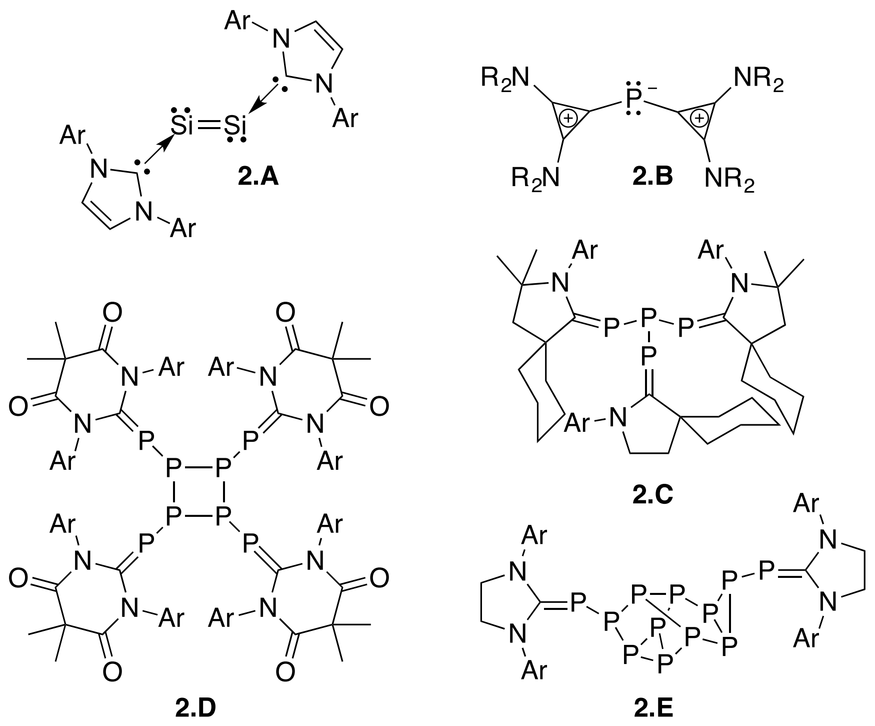


Figure 2.1: Silicon(0) species **2.A** and selected products **2.B–2.E** from P_4 activation by carbenes, demonstrating the diverse assortment of clusters obtained.

The steric environment of carbenes also plays a pivotal role in isolating reactive species. Indeed, when the bulky and rigid CAAC **2.F** was introduced,[13] several low valent metal species previously unknown could be isolated.[14] More evidently, its activation of P_4 leads to a linear arrangement **2.G** (Figure 2.2),[15] vastly different when compared to the outcome of the smaller CAAC version product **2.C**. The bulky NHC **2.H**[16] reported by Marko *et al.* also proved to be very effective in several catalytic applications and allowed for the isolation of reactive organometallic complexes.[17] NHC **2.I**[18] which is considered an “extremely sterically shielding” NHC has allowed for the isolation and characterization of coinage metal carbene complexes without any heteroatom stabilization;[19] these type of complexes have been proposed as key intermediates in many catalytic cycles but never before observed. With the appropriate carbene, many proposed intermediates can be isolated and studied in detail.[20] With this better understanding, improvements can be rationally made to catalytic systems.

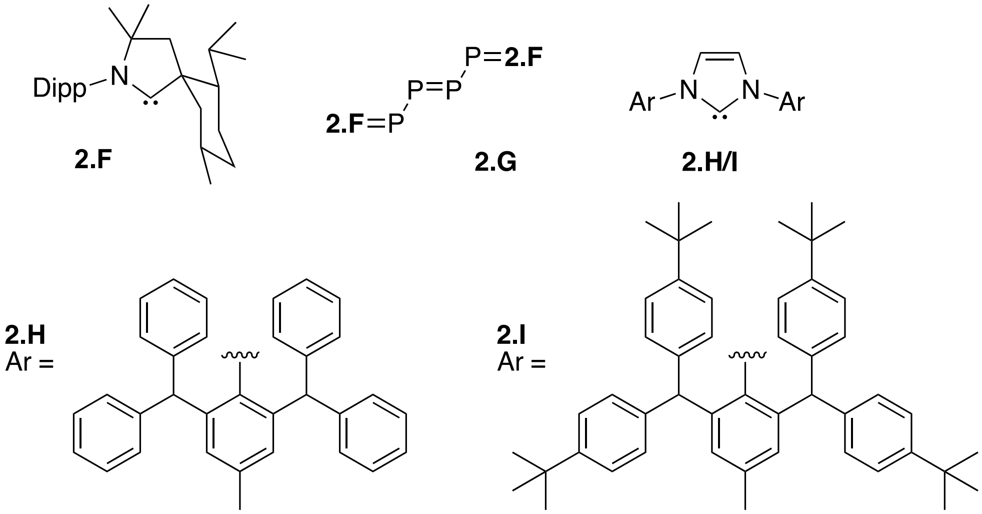


Figure 2.2: Bulky CAAC **2.F** and its P_4 activation product **2.G**. Sterically shielding carbenes **2.H** and **2.I**.

In this chapter, we will use electronic and steric properties to isolate previously unknown compounds based on Group 15 elements. First we demonstrate that steric protection is necessary to isolate the parent phosphenium cation (PH_2^+) and related species. Then we utilize the peculiar electronic properties of the CAAC to isolate four different antimony species in the formal oxidation states of three, two, one, and zero.

A) Parent phosphenium compounds

As outlined in the previous section, the combination of σ-donor and π–acceptor properties of carbenes can stabilize reactive intermediates through delocalization of the electron density. One class of species they have been shown to stabilize is phosphinidenes,[21] the phosphorus analogues to carbenes.[22] So far, these transient species have only been observed in the coordination sphere of a metal[23] or as Lewis base adducts.[24] For the parent phosphinidene (PH), only one metal-stabilized terminal PH complex has been reported,[25] as well as an NHC-PH adduct,[26] but further chemistry was not reported. In contrast, the parent phosphenium ion (PH_2^+), and even any phosphenium salts bearing a hydrogen (PHR^+), have never been observed. This is striking since the chemistry of the PR_2^+ derivatives[27] has been widely studied due to their fascinating coordination chemistry,[28] their reactivity with organic reagents,[29] and their use as building blocks for larger phosphorus clusters.[30] Since the parent PH was isolated with an NHC, we sought to achieve the corresponding PH_2^+ fragment.

The NHC–stabilized parent phosphinidene adduct **2.J** features an inversely polarized CP bond denoted by two forms **A** and **B** (Figure 2.3).[31] The HOMO of **2.J** displays the π back donation of a phosphorus lone pair into the carbene empty orbital. Additionally, the coefficient at P (0.50) is significantly larger than at C (0.05), which suggests that the P lone pair will be the nucleophilic site. These properties should allow for the synthesis of the desired phosphenium compounds upon addition of the appropriate electrophiles.

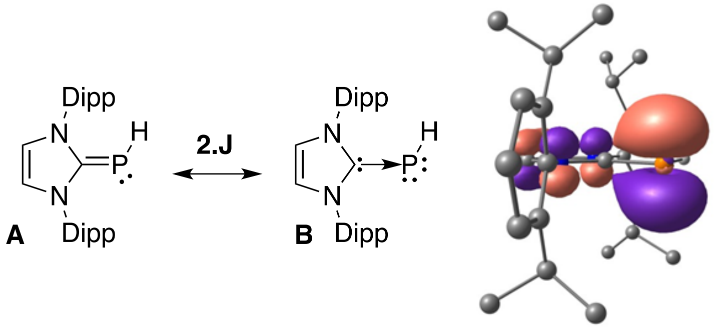


Figure 2.3: Two bonding modes of **2.J** and its HOMO.

Since we presumed that the NHC–PHR^+ and especially PH_2^+ species would be extremely reactive, we chose the aforementioned sterically encumbering NHC **2.H**.

Compound **2.1** was prepared following a slightly modified synthesis described by Grützmacher *et al.*,[26c] and isolated in 87% yield. The ^{31}P NMR spectrum shows a doublet at –134.5 ppm (J_{PH} = 172 Hz), which is comparable to **2.J** (–136.7 ppm, J_{PH} = 164 Hz). An X-ray diffraction study of **2.1** confirmed its structure, and as desired the PH moiety lays inside the protective pocket of the bulky substituents (Figure 2.4).

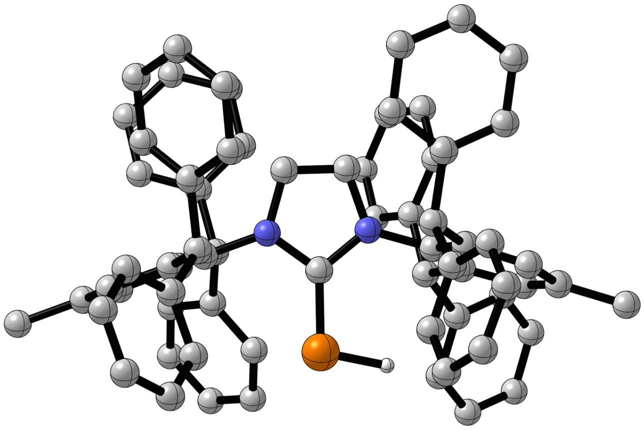
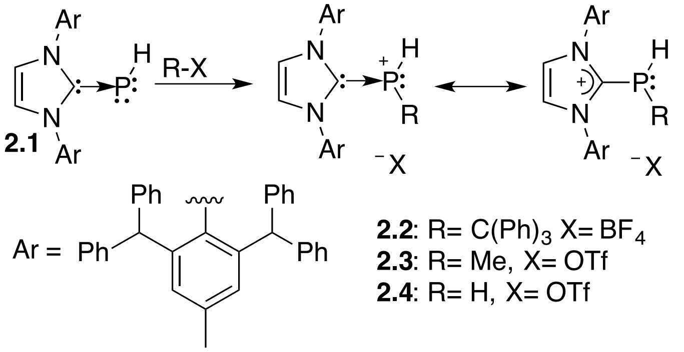


Figure 2.4: Molecular view of **2.1** in the solid state with hydrogen atoms (except P–H) and solvent molecules omitted for clarity.

To test the validity of preparing phosphenium adducts bearing a hydrogen atom, we first chose the bulky triphenylcarbenium as the electrophile (Scheme 2.1). A rapid reaction occurred upon mixing **2.1** and the tetraflouroborate salt [(Ph_3C^+)(BF_4^-)]. After 5 minutes, the ^{31}P NMR spectrum showed a single doublet at –49.4 ppm (J_{PH} = 278 Hz). After work-up compound **2.2** was isolated as a white solid in 89% yield. Next, we used the smaller electrophile MeOTf. Again, the reaction with **2.1** was rapid and lead cleanly to **2.3**, as a white solid in 87% yield (^{31}P = –86.3 ppm, J_{PH} = 240 Hz). To verify the solid-state structures, single crystals of **2.2** and **2.3** were grown and subjected to an X-ray diffraction study (Figure 2.5). The structures confirmed the cationic nature of the products. For **2.2** a drastic lengthening of the C_{carb}–P (1.845(2) Å) bond compared to **2.1**

(1.755(4) Å) occurred. These compounds are sensitive to air and moisture, but are thermally stable and can be stored in the solid state for months under an inert atmosphere.



Scheme 2.1: Synthesis of phosphenium ions **2.2**, **2.3**, and **2.4**.

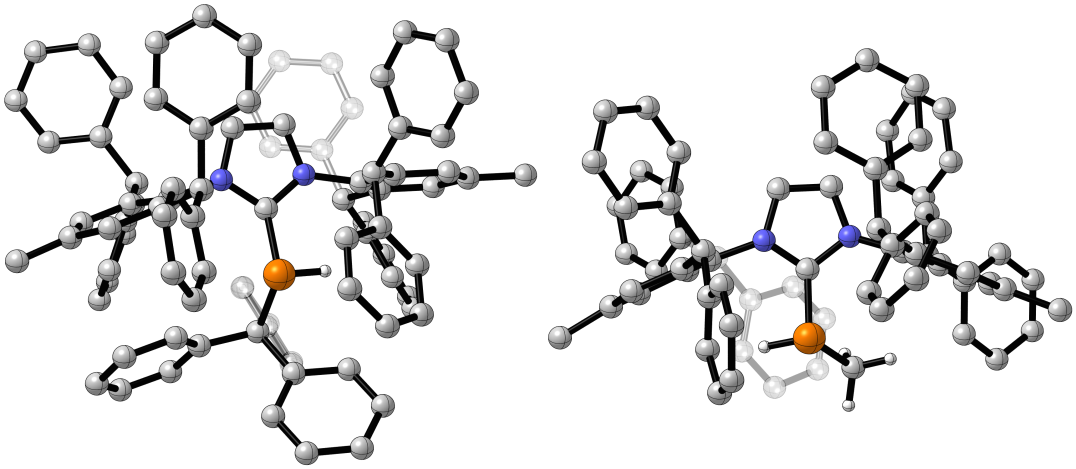


Figure 2.5: Molecular view of **2.2** (left) and **2.3** (right) in the solid state with hydrogen atoms (except P–H and P–CH_3), solvent molecules, and anions omitted for clarity.

Following the successful isolation of **2.2** and **2.3**, we attempted the synthesis of the parent derivative. HOTf was added to a solution of **2.1**, and after work-up, compound **2.4** was isolated as a white powder in 85% yield (Scheme 2.1). A triplet is observed in the ^{31}P NMR spectrum (Figure 2.6) at –166.6 ppm (J_{PH} = 223 Hz), which collapses into a singlet upon proton decoupling, indicating the presence of a PH_2 fragment. Single colorless crystals were grown by vapor diffusion of pentane into a saturated chloroform solution. The solid-state structure validated the ionic nature of **2.4** (Figure 2.6). Due to the crystal packing, it was not possible to locate the hydrogen atoms on phosphorus. However, the presence of the anion along with a terminal P atom in conjunction with the NMR data confirms the formulation. The C_{carb}–P bond extends to 1.840(4) Å, indicating a decrease in the bond order.

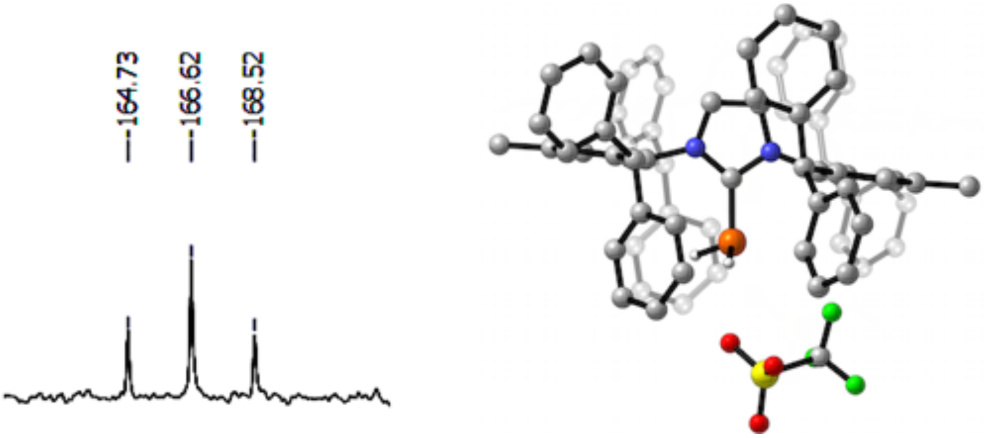


Figure 2.6: Left: ^{31}P NMR spectrum of **2.4**. Right: Molecular view of **2.4** in the solid state with hydrogen atoms omitted for clarity.

Computational methods were performed to gain a better understanding of the bonding in **2.4**. The natural bond orbital (NBO) analysis was performed at the M06-2X/ 6-311+G(2d,p)//M06-2X/6-31G(d) level of theory (Figure 2.7). The phosphorus center forms three bonds [C_{carb}–P σ (a) and two P–H σ (b and c)] and has a lone pair of electrons (d). The calculations indicated no π-electron density between the carbene carbon atom and the phosphorus atom. The NBO charges of C_{carb} and P in **2.4** are 0.23 and 0.62e, respectively. Accordingly, delocalization of the positive charge over the NHC fragment only slightly contributes to the structure. The Wiberg bond index (WBI) for the C_{carb}–P was calculated to be 0.95, which supports the C_{carb}–P dative bond nature. These computational studies support the carbene-stabilized phosphenium model.

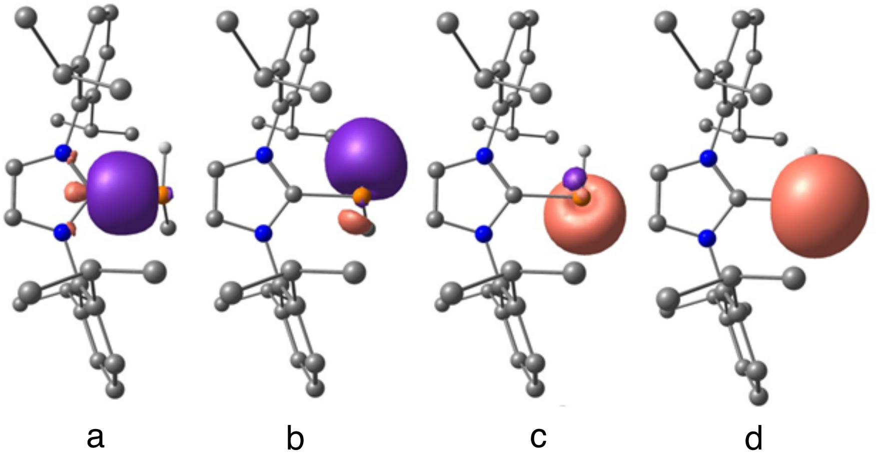
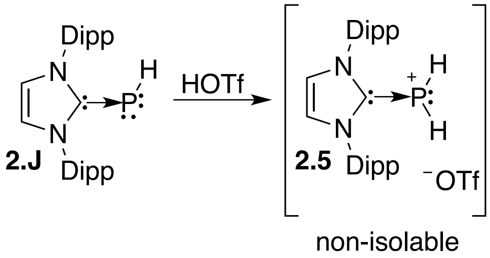


Figure 2.7: NBOs of the C_{carb}–PH_2 fragment of a simplified model of **2.4**: a) C_{carb}–P σ; b) P–H σ; c) P–H σ; d) lone pair of electrons at P.

The isolation and structural characterization of these compounds indicate that parent phosphenium salts can be readily isolated. Therefore, we turned our attention to using the much less bulky NHC–PH **1.J**, which features a Dipp substituent. Indeed, following the same procedure as before (Scheme 2.2), compound **2.5** can be observed in solution by ^{31}P NMR spectroscopy (t, –165.3 ppm, J_{PH} = 220 Hz). However attempts to isolate it failed as it rapidly decomposes in the absence of solvent. Evidently, the steric protection is vital.



Scheme 2.2: Observation of **2.5** from **2.J**.

B) Parent phosphinidene complexes

Having shown that the P center of **2.1** readily reacts with electrophiles, we were curious to investigate its coordination ability. Although a few reports on substituted NHC-phosphinidenes (PR) coordinating to metals exist,[24c, 24e, 32] no attempts have been made with the parent analogue. We first reacted **2.1** with diiron nonacarbonyl [$Fe_2(CO)_9$], and a doublet a –96.4 ppm (J_{PH} = 208 Hz) was observed by ^{31}P NMR spectroscopy. This compound was isolated as an orange solid in 80% yield, and single crystals were grown by vapor diffusion of hexanes into a chloroform solution. The solid-state structure of **2.6** confirmed the coordination of the phosphorus to the metal (Figure 2.8), and an elongation of the C_{carb}–P to 1.828(3) Å. Interestingly, the NBOs of **2.6** show that the P center still possesses a second lone pair available for bonding (Figure 2.8), but the addition of excess $Fe_2(CO)_9$ did not lead to further coordination.

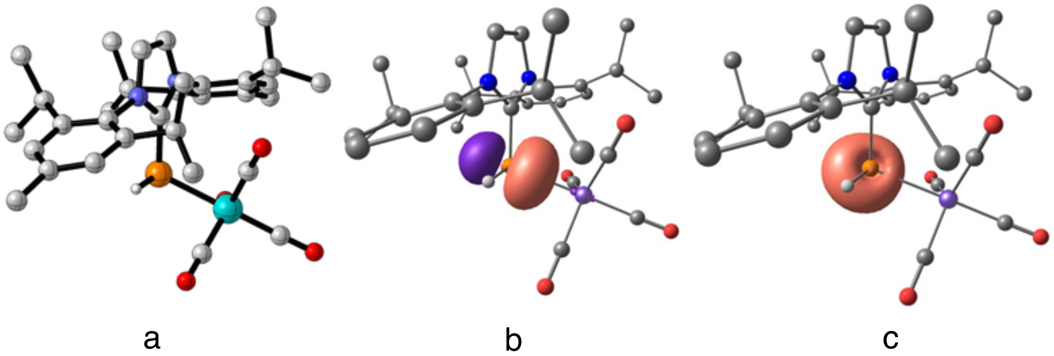
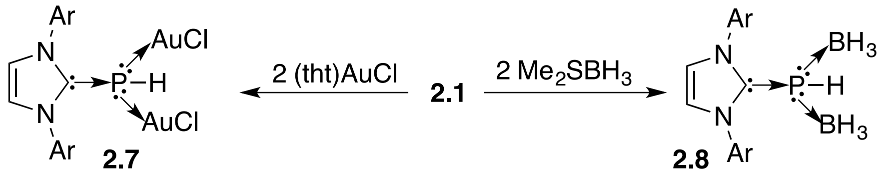


Figure 2.8: a) Molecular view of **2.6** in the solid state with hydrogen atoms (except P–H) and the phenyl groups on the 2,6-dibenzhydryl-4-methylpenyl omitted for clarity. Selected NBOs of a simplified model of **2.6**: b) P–Fe σ; c) the remaining lone pair of electrons on P.

The lack of further reactivity could be attributed to the bulky iron complex combined with the bulky NHC. To test this assumption, we reacted **2.1** with excess of the singly ligated and linear (tht)AuCl. By ^{31}P NMR spectroscopy, a similar shift to **2.6** was observed at –92.2 ppm (d, J_{PH} = 373 Hz). To clarify the bonding situation, single crystals were grown and subjected to an X-ray diffraction study (Figure 2.9). The solid-state structure revealed that indeed both of the lone pairs were be utilized, as the bis-metal complex **2.7** was formed. As has been the case, the C_{carb}–P bond elongated upon coordination to 1.827(7) Å.



Scheme 2.3: Synthesis of **2.7** and **2.8** from **2.1**.

To further validate the availability of both lone pairs, the coordination to a main group Lewis acid was explored. A fast reaction occurred when $Me_2S–BH_3$ was added to a solution of **2.1** (Scheme 2.3). The ^{31}P NMR spectrum displayed a broad doublet at –39.2 ppm (J_{PH} = 330 Hz) and the ^{11}B NMR spectrum showed a broad peak at –37.0 ppm. The solid-state structure revealed the bis(borane) adduct **2.8** (Figure 2.9).

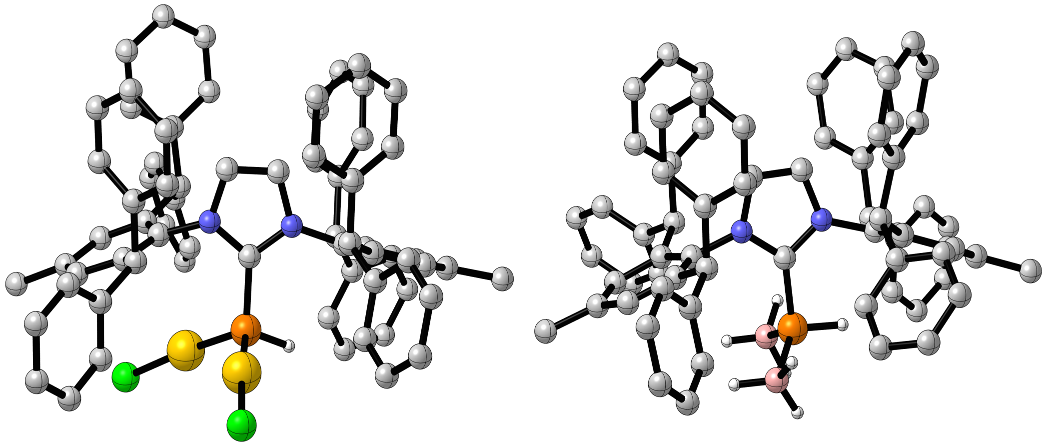


Figure 2.9: Molecular view of **2.7** (left) and **2.8** (right) in the solid state with hydrogen atoms (except P–H and B–H) and solvent molecules omitted for clarity.

The NBO analyses of **2.7** and **2.8** were performed to gain insight into their bonding situations. Selected NBO charges and WBIs are depicted in Figure 2.10. In compound **2.7** the P is almost neutral (–0.01 a.u.), whereas it is significantly positively charged in **2.8** (+0.79 a.u.); this might be attributed to the Lewis acidic character of the BH_3. The WBIs of the P–Au bonds in **2.7** (0.53 and 0.52) are much lower than the P–B of **2.8** (0.85 and 0.84). This stronger bonding between the P–BH_3 compared to the P–Au is also observed experimentally where **2.7** slowly decomposes overnight in solution, while **2.8** is stable over months.

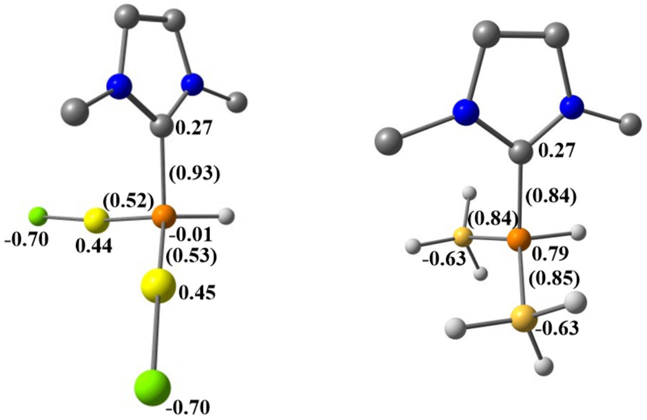


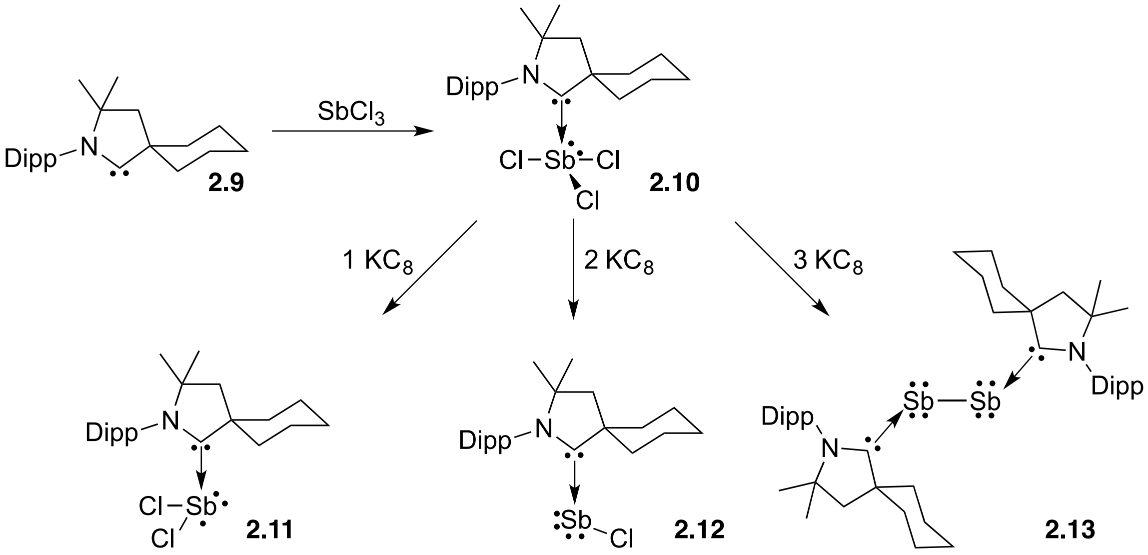
Figure 2.10: Selected NBOs and WBIs (in parentheses) of simplified models of **2.7** (left) and **2.8** (right).

The steric environment plays a role in these types of compounds. Depending on the metal precursor, the PH moiety is able to utilize one or both of its lone pairs to bind one or two metals. Its nucleophilic nature is apparent by its reaction with BH_3 giving the corresponding bis(borane) adduct.

C) CAAC-stabilized antimony adducts

As illustrated above, NHCs are useful in isolating reactive species based on phosphorus. They have been employed to stabilize an array of main group element derivatives featuring unusual binding modes, atoms in low oxidation states, and paramagnetic species.[3] Indeed, the isolation of mono- and diatomic main group species in their zero oxidation state capped by carbenes has flourished with the reports on Group 13,[33] 14,[34] and 15 elements. NHC-stabilized N_2,[35] P_2,[36] and As_2[37] are the representative Group 15 elements. Although the analogous NHC-antimony and bismuth derivatives are predicted to be stable,[38] their attempted isolation was reported to fail.[39] Typically the NHC-ECl_3 compound is reduced with an excess of KC_8 and the corresponding NHC-E-E-NHC product is obtained. With NHC-$SbCl_3$ the reduction was reported to lead to free carbene and elemental Sb particles.[40] Since CAACs have been able to stabilize species where NHCs cannot, we attempted to prepare the corresponding CAAC-$SbCl_3$ and study its stepwise reduction process.

The addition of $SbCl_3$ to a diethyl ether solution of CAAC **2.9**, gave the desired compound **2.10** as a white solid in 94% yield (Scheme 2.4). The ^{13}C NMR spectrum of CAAC-$SbCl_3$ complex **2.10** shows the carbene signal shifted drastically upfield (228.4 ppm) compared to free CAAC **2.9** (316.1 ppm). Single crystals of **2.10** were grown by a slow evaporation of a concentrated THF solution. The X-ray diffraction study confirms the four-coordinate nature of the antimony center (Figure 2.11), and the distorted seesaw geometry resembles that of the Group 15 homologues NHC-PCl_3, NHC-$AsCl_3$, and NHC-$BiCl_3$.



Scheme 2.4: Synthesis of CAAC–SbCl$_3$ **2.10** and its stepwise reduction with KC$_8$ affording CAAC–Sb complexes **2.11**–**2.13**.

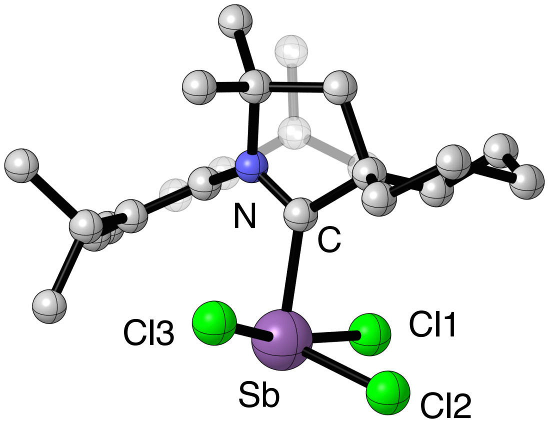


Figure 2.11: Molecular view of **2.10** in the solid state with hydrogen atoms and solvent molecules omitted for clarity.

First, one equivalent of KC$_8$ and **2.10** were stirred in benzene, yielding a golden colored solution. Despite several efforts, single crystals could not be obtained. This NMR-silent compound was EPR active, demonstrating its paramagnetic nature (Figure 2.12a). Two close energy minima **2.11a** and **2.11b** were located with open-shell calculations at the uM05-2X/def2-SVP//uM05-2X/def2-TZVP level of theory. **2.11a** comes from the formal abstraction of Cl2 and **2.11b** results from the formal abstraction of Cl1 or Cl3, from **2.10**. Interestingly, DFT calculations reveal that **2.11a** and **2.11b** have very different Mulliken-spin density distributions. In **2.11a** the antimony is in a distorted T-shaped environment (Figure 2.12c), with most of the spin density located on antimony (90.7%), and minor contributions from the two chlorine atoms (4.6 and 3.9%). For **2.11b** a trigonal pyramidal geometry (Figure 2.12d) is seen around the antimony, and the spin density is mainly located on the carbene center (58.7%), with contributions from nitrogen (22.1%), antimony (11.1%), and only one chlorine atom (7.3%). Although antimony contributes to both structures, its calculated hyperfine coupling is negligible (**2.11a**: 0.004; **2.11b**: 0.040 G), which is reminiscent to the previously reported Sb-centered radicals ($Ar_3Sb\bullet^{+}$[41] and $ArSbSbAr\bullet^{-}$[42]) where the absence of coupling was also observed. Thus, the other active nuclei will be responsible for the observed EPR spectrum. For **2.11a**, which has contribution from two nearly equivalent chlorine nuclei (S = 3/2) a septet is expected. Compound **2.11b** should give a sextet due to the coupling with one chlorine and one nitrogen (S = 1). From the experimental EPR spectrum, the observed radical is most likely **2.11a**, with the spin density mostly on the antimony. The simulated EPR spectrum **2.11** has the following set of hyperfine coupling constants: $a(^{121}Sb) = 0.003$ (57%), $a(^{123}Sb) = 0.003$ (43%), and $a(^{35}Cl) = 4.472$, $a(^{35}Cl) = 4.472$ G (calculated values: $a(^{121}Sb) = 0.004$ (57%), $a(^{123}Sb) = 0.004$ (43%), $a(^{35}Cl) = 3.217$, $a(^{35}Cl) = 3.533$ G). This result also agrees with coupling to two chlorine nuclei and a negligible amount to nitrogen, further supporting structure **2.11a**.

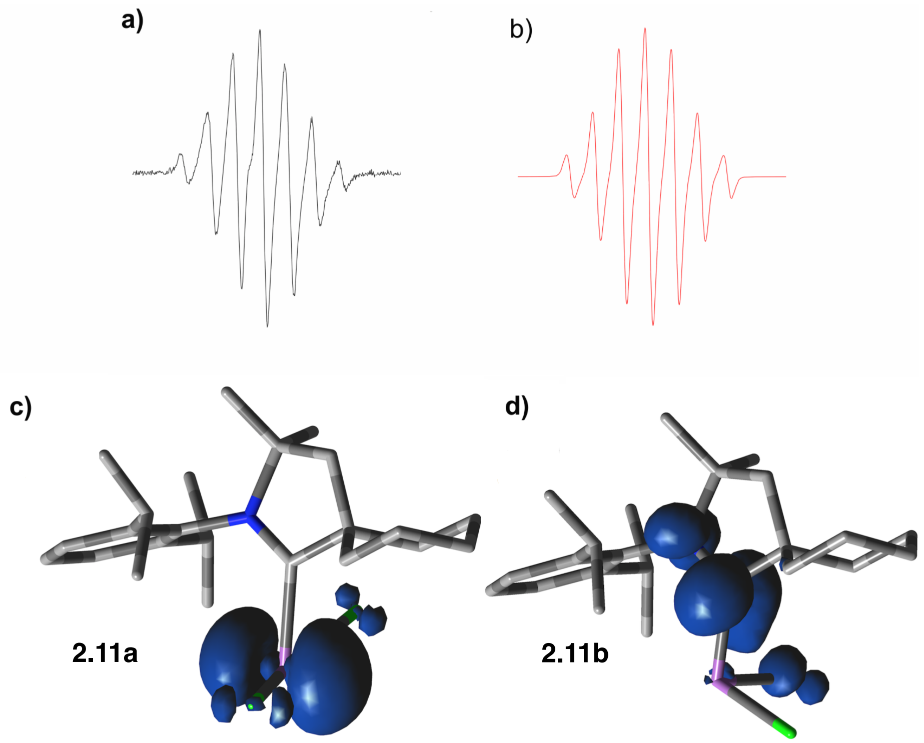


Figure 2.12: a) EPR spectrum of **2.11** in benzene at room temperature; b) simulated EPR spectrum; c), d) SOMO of **2.11a** and **2.11b**, respectively.

Next we attempted the second reduction; addition of two equivalents of KC_8 to a solution of **2.10** produced a yellow colored solution. After work-up, compound **2.12** was isolated as yellow crystals in 26% yield (Scheme 2.4). The carbene ^{13}C NMR signal (241.3 ppm) appeared downfield compared to **2.10** (228.4 ppm). An X-ray diffraction study showed that a double reduction had occurred and only one chlorine atom remained bound to the antimony center (Figure 2.13). Compound **2.12** features a severely bent C–Sb–Cl fragment (100.77(13)º), and the Sb–C bond (2.082(5) Å) is shorter compared to the precursor **2.10** (2.223(3) Å).

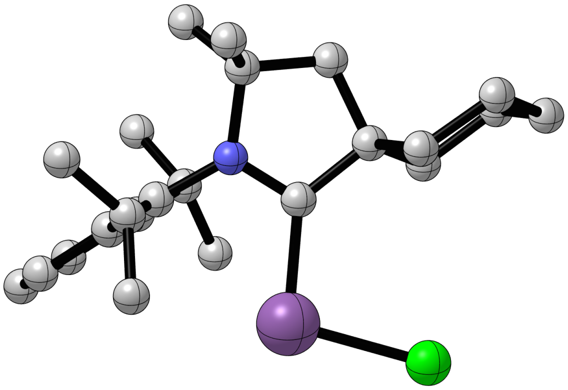


Figure 2.13: Molecular view of **2.12** in the solid state with hydrogen atoms omitted for clarity.

To gain insight into the bonding situation, calculations were performed at the M05-2X/def2-SVP//M05-2X/def2-TZVP level of theory. The WBI for the Sb–C bond is 1.282, which indicates only a partial double-bond character. The localized molecular orbitals (LMOs) (Figure 2.14) show that the Sb–C bond results from the carbene lone pair donation to Sb (a), and some π back donation comes from one of the Sb lone pair orbitals (b), which has predominantly p-character (4.22% s, 95.65% p, 0.12% d); the other Sb lone pair orbital (c) is mostly s-character (84.02% s, 15.96% p, 0.01% d).

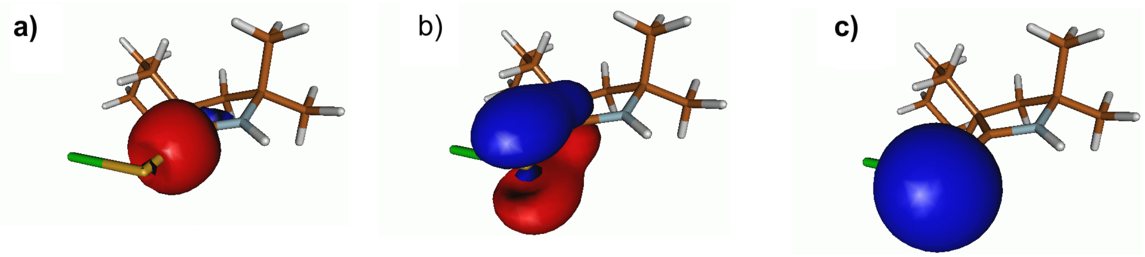


Figure 2.14: LMOs of a simplified model of **2.12**: a) Sb–C σ; b) π back donation from one of the Sb lone pair to the empty carbene orbital; c) Sb lone pair orbital.

Following the successful double reduction, we next attempted the full reduction. Mixing three equivalents of KC_8 and **2.10** caused a deep purple solution (Scheme 2.4). Storing the toluene solution at –20 ºC resulted in purple blocks that were isolated in 45%

yield. An X-ray diffraction analysis of the blocks revealed the diatomic Sb compound **2.13** (Figure 2.15). In the solid state, **2.13** features an anticlinical twisted-bent geometry. The Sb–C bond lengths (2.084(11) and 2.088(10) Å) are similar to **2.12** and have a WBI of only 1.234. The Sb–Sb bond length (2.8125(10) Å) compares well to other Sb–Sb single bonds found in distibanes[43] and the Sb–Sb bond has predominantly 5p character (8.98% s, 90.62% p, 0.36% d). Similarly to **2.12**, the other three LMOs are the carbene lone pair donation to Sb, the empty p-orbital of the carbene carbon accepting π back donation from the Sb lone pair orbital (0.44% s, 99.38% p, 0.15% d), and the remaining Sb lone-pair orbital comprised mostly of s character (79.28% s, 20.67% p, 0.05% d).

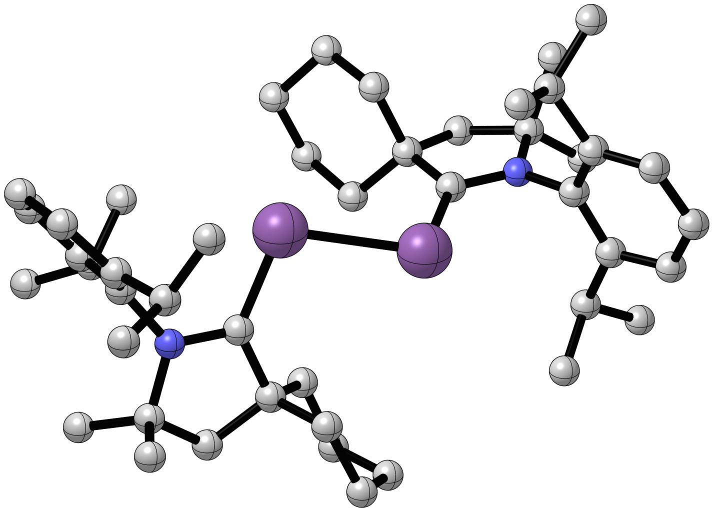


Figure 2.15: Molecular view of **2.13** in the solid state with hydrogen atoms omitted for clarity.

Conclusion

In this chapter, the isolation of Group 15 elements in previously unknown bonding motifs has been achieved by the use of appropriate carbene fragments. In the first section, parent phosphenium compounds were isolated. We demonstrated that without the steric bulk of the NHC **2.H** the PH_2^+ fragment was unstable. Despite its large steric bulk, we demonstrated that **2.H** is flexible enough to allow reactivity at phosphorus with large electrophiles and transition metal complexes.

Finally, we showed that the previously unattainable carbene-stabilized low valent antinomy compounds could be isolated and structurally characterized. Utilizing a CAAC instead of an NHC allowed for a stepwise reduction process. With NHC-diatomic species, the singly and doubly reduced intermediate compounds have never been documented. The stepwise reduction of a single carbene antimony(III) adduct allowed for the preparation of three different antimony species in the formal oxidation states of two, one, and zero. This is a very rare example of a single ligand stabilizing a metal or a metalloid center in four different oxidation states.

As a whole, the characterization of these novel compounds gives insight into isolating other unknown fragments. Both steric control and electronic properties need to be considered when choosing the appropriate carbene as the stabilizing entity.

Chapter 2 has been adapted from materials published in R. Kretschmer, D. A. Ruiz, C. E. Moore, A. L. Rheingold, G. Bertrand, *Angew. Chem. Int. Ed.* **2014**, *53*, 8176–8179 and L. Liu, D. A. Ruiz, F. Dahcheh, G. Bertrand, *Chem. Commun.* **2015**, *51*, 12732–12735. The dissertation author was co-primary investigator of these papers.

Appendix: Experimental Section

1) General Information

All manipulations were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under argon. ^{1}H, ^{13}C, ^{11}B, and ^{31}P NMR spectra were recorded on a Varian VX 500, Bruker 300 and Jeol 500 spectrometer at 25 °C. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *sept* = septet, *m* = multiplet, *br* = broad signal. Chemical shifts are given in ppm and coupling constants *J* are given in Hz. EPR spectra were obtained using an X-band Bruker E500 spectrometer. Field calibration was accomplished by using a standard of solid 2,2-diphenyl-1-picrylhydrazyl (DPPH), g = 2.0036.[44] Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo-Kα radiation ($\lambda = 0.71073$ Å) at the UC San Diego Crystallography Facility. Mass spectra were performed at the UC San Diego Mass Spectrometry Laboratory. Melting points were measured with an electrothermal MEL-TEMP apparatus.

2) General Procedures

Preparation of 2.1: [**2.H**-H][Cl] (1.00 g, 1.05 mmol) and NaPCO•(1,4-dioxane)$_{2.5}$ (0.40 mg, 1.55 mmol) were dissolved in 50 mL of THF and heated to 80 ºC overnight. After cooling to room temperature, the volatiles were removed under vacuum. The residue was extracted with 60 mL of benzene. The solvent was removed under vacuum leading to 0.87 mg (87%) of an off white solid. Single colorless crystals were grown by slow evaporation of a saturated ether solution. M.p.: 278–280 ºC. IR (solid, cm^{-1}) ν_{max} 2291 (P–H). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.46 (m, 8H), 7.26 (m, 12H), 7.13 (m, 12H), 6.90 (s, 4H), 6.87 (m, 8H), 5.61 (s, 4H), 5.09 (s, 2H), 2.26 (s, 6H), 2.10 (d, J_{PH} = 172 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.3 (d, J_{PC} = 81.7 Hz), 143.8, 143.1, 142.4, 139.4, 133.5, 130.7, 130.2, 129.7, 129.5, 128.6, 128.3, 128.1, 126.5, 126.3, 119.0, 51.7, 22.0; ^{31}P NMR (121 MHz, $CDCl_3$): δ = –134.5 (d, J_{PH} = 172 Hz). HRMS: m/z calculated for $[C_{69}H_{58}N_2P]^+$ $(M+H)^+$ 945.4332, found 945.4328.

Preparation of 2.2: **2.1** (100 mg, 0.106 mmol) and $[(Ph_3C^+)(BF_4^-)]$ (35 mg, 0.106 mmol) were dissolved in 5 mL of chloroform. After 5 minutes, the volatiles were removed under vacuum. The residue was washed with 5 mL of diethyl ether and 5 mL of pentane, leading to 120 mg (89%) of a white solid. Colorless crystals were grown by vapor diffusion of pentane into a saturated THF solution. M.p.: 340–345 ºC. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.46-6.24 (br m, 63H), 5.27 (s, 2H), 5.20 (d, J_{PH} = 278 Hz), 2.28 (br s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.5 (d, J_{PC} = 96 Hz), 142.8, 142.7, 141.5, 141.2, 140.7, 132.3, 131.6, 130.8, 130.1-127.2 (broad and overlapping peaks), 67.7 (d, J_{PC} = 39 Hz), 51.9, 22.1; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -49.4 (d, J_{PH} = 278 Hz). HRMS: m/z calculated for $[C_{88}H_{72}N_2P]^+$ $(M)^+$ 1187.5428, found 1187.5431.

Preparation of 2.3: **2.1** (60 mg, 0.063 mmol) was dissolved in 5 mL of benzene and one drop of MeOTf was added to the solution. After 5 minutes, the volatiles were removed under vacuum. The residue was washed with 5 mL of diethyl ether and 5 mL of pentane, leading to 61 mg (87%) of a white solid. Colorless crystals were grown by vapor diffusion of pentane into a saturated chloroform solution. M.p.: 330–335 ºC. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.30-7.22 (m, 24H), 6.97 (m, 4H), 6.89 (m, 8H), 6.82 (m, 8H), 6.02 (s, 2H), 4.97 (s, 2H), 4.89 (s, 2H), 4.06 (dq, J_{PH} = 241 Hz, J_{HH} = 7.6 Hz, 1H), 2.29 (s, 6H), 0.43 (dd, J_{PH} = 7.4 Hz, J_{HH} = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 152.6 (d, J_{PC} = 54 Hz), 142.6, 142.2, 142.1, 141.0, 140.3, 140.2, 140.0, 131.6, 131.2, 129.6, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 127.9, 127.7, 127.6, 126.7, 51.9, 51.6, 22.0, 0.6 (d, J_{PC} = 16 Hz); ^{31}P NMR (121 MHz, CDCl$_3$): δ = -86.3 (d, J_{PH} = 240 Hz). HRMS: m/z calculated for $[C_{70}H_{60}N_2P]^+$ $(M)^+$ 959.4489, found 959.4488.

Preparation of 2.4: **2.1** (50 mg, 0.053 mmol) was dissolved in 5 mL of benzene and one drop of HOTf was added to the solution. After 5 minutes, the volatiles were removed under vacuum. 5 mL of diethyl ether was added to give a clear solution, but upon rigorous stirring a precipitate appeared. The white solid was collected by filtration (49 mg; 85 %). Colorless crystals were grown by vapor diffusion of pentane into a saturated chloroform solution. M.p.: 295–299 ºC. IR (solid, cm^{-1}) ν_{max} 2357, 2302 (P–H). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.29-7.24 (m, 16H), 7.18 (m, 8H), 6.93 (s, 4H), 6.85 (m, 16H), 6.38 (s, 2H), 4.87 (s, 4H), 3.16 (d, J_{PH} = 223 Hz, 2H), 2.30 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 148.0 (d, J_{PC} = 44 Hz), 142.9, 141.5, 140.6, 140.4, 131.7, 129.8, 129.5, 129.3, 129.1, 128.1, 127.8, 127.6, 51.9, 22.1; ^{31}P NMR (121 MHz, CDCl$_3$): δ = –166.6 (t, J_{PH} = 223 Hz). HRMS: m/z calculated for $[C_{69}H_{58}N_2P]^+$ $(M)^+$ 945.4332, found 945.4333.

Observation of 2.5: **2.J** (50 mg, 0.111 mmol) was dissolved in 2 mL of benzene and one drop of HOTf was added to the solution. ^{31}P NMR (121 MHz): δ = –165.3 ppm (t, J_{PH} = 220 Hz).

Preparation of 2.6: **2.1** (50 mg, 0.053 mmol) and $Fe_2(CO)_9$ (15 mg, 0.041 mmol) were dissolved in 5 mL of benzene. After 6 hours, the mixture was filtered and the solvent was removed under vacuum. The residue was washed with 5 mL of pentane, leading to 46 mg

(80%) of an orange solid. Single orange crystals were grown by vapor diffusion of pentane into a saturated THF solution. M.p.: 265–270 ºC. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.23 (m, 20H), 7.11 (m, 12H), 6.85 (s, 4H), 6.69 (m, 8H), 5.55 (s, 4H), 5.06 (s, 2H), 3.22 (d, J_{PH} = 208 Hz, 1H), 2.22 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 216.3 (d, J_{PC} = 3 Hz), 143.0, 142.7, 141.8, 140.9, 132.2, 131.6, 130.2, 129.6, 128.4, 128.3, 126.8, 127.7, 50.9, 21.9; ^{31}P NMR (121 MHz, CDCl$_3$): δ = –96.4 (d, J_{PH} = 208 Hz). HRMS: m/z calculated for $[C_{73}H_{58}FeN_2O_4P]^+$ $(M+H)^+$ 1113.3480, found 1113.3470.

Preparation of 2.7: **2.1** (50 mg, 0.053 mmol) and (tht)AuCl (37 mg, 0.115 mmol) were dissolved in 5 mL of benzene. After 5 minutes, 3 mL pentane was added which induced a precipitate. The mixture was filtered and the solid was washed with 2 mL benzene. 37 mg (53%) of a light yellow solid was obtained. Single crystals were grown by vapor diffusion of pentane into a saturated chloroform solution. M.p.: 270 ºC. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.55 (m, 4H), 7.40 (s, 3H), 7.37-7.31 (m, 14H), 7.22-7.08 (m, 12H), 7.01 (m, 4H), 6.78 (m, 4H), 6.70 (m, 4H), 5.51 (m, 3H), 5.29 (d, J_{PH} = 373 Hz, 1H), 5.12 (2, 2H), 2.37 (s, 3H), 2.34 (br s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 148.0 (d, J_{PC} = 16.5 Hz), 143.0, 142.9, 142.8, 147.8, 141.6, 141.5, 140.4, 140.2, 131.9, 131.8, 131.0, 130.9, 129.4, 129.1, 129.0, 128.8, 128.5, 128.1, 127.9, 127.8, 127.7, 127.4, 127.2, 126.9, 125.9, 52.3, 52.2, 22.2, 22.1; ^{31}P NMR (121 MHz, CDCl$_3$): δ = –91.2 (d, J_{PH} = 373 Hz). HRMS: m/z calculated for $[C_{69}H_{56}Au_2N_2P]^+$ $(M-2HCl+H)^+$ 1337.3507, found 1337.3483.

Preparation of 2.8: **2.1** (50 mg, 0.053mmol) was dissolved in 5 mL of THF and two drops of Me_3S-BH_3 were added to the solution. After 5 minutes, 3 mL of pentane was added which induced a precipitate. The mixture was filtered and the solid was washed with 2 mL pentane. 46 mg (89%) of a colorless solid was obtained. Colorless single crystals were grown by vapor diffusion of pentane into a saturated THF solution. M.p.: 257 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35-7.24 (m, 20H), 7.09 (m, 12H), 6.85 (s, 4H), 6.71 (m, 8H), 5.44 (s, 4H), 4.88 (dm, J_{PH} = 330 Hz, 1H), 4.86 (s, 2H), 2.25 (s, 6H), 1.13-0.75 (br, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.1 (d, J_{PC} = 14 Hz), 143.9, 142.1, 142.0, 141.4, 130.9, 130.7, 129.4, 128.5, 127.0, 126.9, 124.8, 51.4, 22.1; ^{11}B NMR (96 MHz, $CDCl_3$): δ = –37.0 (br); ^{31}P NMR (121 MHz, $CDCl_3$): δ = –39.2 (br d, J_{PH} = 330 Hz). HRMS: m/z calculated for $[C_{69}H_{62}B_2N_2P]^+$ $(M-H^-)^+$ 971.4852, found 971.4841.

Preparation of 2.10: A diethyl ether solution (40 mL) of CAAC **2.9** (1.5 g, 4.6 mmol) was placed in a –78 ºC cold bath. In a second flask, $SbCl_3$ (1.2 g, 5.3 mmol) was dissolved in 15 mL of diethyl ether. The $SbCl_3$ solution was added slowly via cannula to the CAAC solution. A white precipitate immediately appeared. The suspension was warmed to room temperature, and stirred for an additional 3 hours. The solvent was filtered off, the solid was washed with 30 mL of diethyl ether, and dried under vacuum. **2.10** was obtained as a white solid (2.4 g, 94% yield). Single crystals were grown by a slow evaporation of a concentrated THF solution. M.p.: 180 ºC (dec.). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.04 (m, 1H), 6.98 (d, J = 7.7 Hz, 2H), 3.22 (m, 2H), 3.06 (sept, J = 6.5 Hz, 2H), 1.96 (m, 2H), 1.65 (s, 2H), 1.61 (m, 2H), 1.56 (d, J = 6.5 Hz, 6H), 1.47 (m, 2H), 1.33 (m, 1H), 1.08 (s, 6H), 0.99 (m, 2H), 0.95 (d, J = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, C_6D_6): δ = 228.4 (C–Sb), 146.6 (C_q), 131.8 (C_q), 131.7 (CH_{Ar}), 126.7 (CH_{Ar}), 83.1 (C_q), 64.9 (C_q), 46.6 (CH_2), 37.4 (CH_2), 29.2, 28.1, 27.4, 26.1, 24.7 (CH_2), 22.7 (CH_2).

Preparation of 2.11, 2.12, and 2.13: One, two, and three equivalents of KC_8 were added in portions over 10 minutes to a stirred toluene solution (5 mL) of **2.10** (200 mg, 0.36 mmol). The mixture was stirred for 2 to 3 hours, and then the salts were filtered off.

Then, the solution was concentrated and stored at –20 ºC. **2.12**: Yellow crystals suitable for an X-ray diffraction study were formed (45 mg, 26% yield). M.p.: 155 ºC (dec.). ^{1}H NMR (500 MHz, toluene-d8): δ = 7.06 (m, 1H), 6.93 (d, *J* = 7.7 Hz, 2H), 3.06 (m, 2H), 2.82 (sept, *J* = 6.5 Hz, 2H), 1.86 (s, 2H), 1.80 (m, 2H), 1.67 (m, 2H), 1.48 (d, *J* = 6.5 Hz, 6H), 1.20-1.08 (m, 8H), 0.98 (s, 6H); ^{13}C NMR (125 MHz, toluene-d_8): δ = 241.3 (C–Sb), 147.7 (C_q), 132.2 (C_q), 131.1 (CH_{Ar}), 127.3 (CH_{Ar}), 82.2 (C_q), 65.4 (C_q), 47.0 (CH_2), 38.1 (CH_2), 30.0, 29.3, 28.7, 25.5, 25.2 (CH_2), 23.8 (CH_2). **5**: Purple block crystals suitable for an X-ray diffraction study were formed (73 mg, 45% yield). M.p.: 134 ºC (dec.); ^{1}H NMR (500 MHz, C_6D_6): δ = 7.09 (t, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 2H), 3.03 (m, 2H), 2.84 (sept, *J* = 6.6 Hz, 2H), 1.80 (s, 2H), 1.64 (m, 4H), 1.52 (d, *J* = 6.6 Hz, 6H), 1.43 (m, 2H), 1.20 (m, 2H), 1.10 (d, *J* = 6.6 Hz, 6H), 0.97 (s, 6H); ^{13}C NMR (125 MHz, C_6D_6): δ = 233.1 (C–Sb), 148.0 (C_q), 137.1 (C_q), 129.2 (CH_{Ar}), 126.0 (CH_{Ar}), 72.7 (C_q), 61.7 (C_q), 49.7 (CH_2), 39.2 (CH_2), 30.0, 29.3, 29.2, 25.2, 23.7 (CH_2), 23.4 (CH_2).

3) Crystallographic Data

Compound	**2.1**
Empirical Formula	$C_{73}H_{67}N_2OP$
Formula weight	1019.26
Crystal system	Orthorhombic
Space group	Pna21
a(Å)	18.9194(13)
b(Å)	14.8964(11)
c(Å)	20.0103(14)
a(deg)	90.00
b(deg)	90.00
g(deg)	90.00
V(Å^3)	5639.5(7)
Z	4
d(calc) gcm^{-3}	1.200
R(int)	0.0870
μ, mm^{-1}	0.097
Total data	9816

$>2\sigma(F_O^2)$	6953
Variables	699
R ($>2\sigma$)	0.0589
R_w	0.1202
GOF	1.052

Compound	**2.2**
Empirical Formula	$C_{88}H_{72}BF_4N_2P$
Formula weight	1275.26
Crystal system	Triclinic
Space group	P-1
a(Å)	13.7202(8)
b(Å)	16.4329(11)
c(Å)	19.0854(12)
a(deg)	74.147(2)
b(deg)	78.554(2)
g(deg)	81.404(2)
V(Å^3)	4036.3(4)
Z	2
d(calc) gcm^{-3}	1.049
R(int)	0.0527
μ, mm^{-1}	0.085
Total data	14228
$>2\sigma(F_O^2)$	10958
Variables	869
R ($>2\sigma$)	0.0559
R_w	0.1498
GOF	1.072

Compound	**2.4**
Empirical Formula	$C_{71}H_{58}F_6N_2O_7PS_2$
Formula weight	1260.28
Crystal system	Triclinic
Space group	P-1
a(Å)	14.4808(11)
b(Å)	14.6435(11)
c(Å)	15.4095(10)
a(deg)	83.039(2)
b(deg)	84.164(2)
g(deg)	77.715(2)
V(Å^3)	3159.5(4)
Z	2
d(calc) gcm^{-3}	1.325
R(int)	0.0398

μ, mm^{-1}	0.184
Total data	11126
$>2\sigma(F_O^2)$	9434
Variables	983
R (>2σ)	0.0527
R_w	0.1251
GOF	1.068

Compound	**2.6**
Empirical Formula	$C_{73}H_{57}FeN_2O_4P$
Formula weight	1113.03
Crystal system	Monoclinic
Space group	P21/n
a(Å)	12.6626(8)
b(Å)	18.3247(11)
c(Å)	25.5405(15)
a(deg)	90.00
b(deg)	101.719(2)
g(deg)	90.00
V($Å^3$)	5802.8(6)
Z	4
d(calc) gcm^{-3}	1.274
R(int)	0.0868
μ, mm^{-1}	0.341
Total data	10031
$>2\sigma(F_O^2)$	6713
Variables	736
R (>2σ)	0.0567
R_w	0.1433
GOF	1.042

Compound	**2.7**
Empirical Formula	$C_{69}H_{57}Au_2Cl_2N_2P$
Formula weight	1409.97
Crystal system	Monoclinic
Space group	P21/c
a(Å)	15.4817(9)
b(Å)	18.0766(10)
c(Å)	24.4404(14)
a(deg)	90.00
b(deg)	98.019(2)
g(deg)	90.00
V($Å^3$)	6772.9(7)
Z	4

d(calc) gcm^{-3}	1.383
R(int)	0.0520
μ, mm^{-1}	4.467
Total data	11927
>2σ(F_O^2)	10722
Variables	713
R (>2σ)	0.0447
R_w	0.1246
GOF	1.106

Compound	**2.8**
Empirical Formula	$C_{69}H_{63}B_2N_2P$
Formula weight	972.80
Crystal system	Monoclinic
Space group	P21/c
a(Å)	13.5874(18)
b(Å)	17.073(2)
c(Å)	24.447(3)
a(deg)	90.00
b(deg)	105.718(3)
g(deg)	90.00
V(Å^3)	5459.0(12)
Z	4
d(calc) gcm^{-3}	1.184
R(int)	0.1172
μ, mm^{-1}	0.095
Total data	9604
>2σ(F_O^2)	5654
Variables	697
R (>2σ)	0.0571
R_w	0.1231
GOF	1.020

Compound	**2.10**
Empirical Formula	$C_{25}H_{39}Cl_3NO_{0.5}Sb$
Formula weight	589.67
Crystal system	Monoclinic
Space group	P 1 21/c 1
a(Å)	9.716(3)
b(Å)	14.820(4)
c(Å)	19.044(5)
a(deg)	90.00
b(deg)	103.359(6)
g(deg)	90.00
V(Å^3)	2557.9(12)

Z	4
d(calc) gcm^{-3}	1.468
R(int)	0.0501
μ, mm^{-1}	1.350
Total data	24431
$>2\sigma(F_O^2)$	1208
R ($>2\sigma$)	0.0300
R_w	0.0570
GOF	1.010

Compound	**2.12**
Empirical Formula	$C_{23}H_{35}ClNSb$
Formula weight	482.72
Crystal system	Monoclinic
Space group	P 1 2/c 1
a(Å)	23.450(2)
b(Å)	10.9798(8)
c(Å)	19.3771(15)
a(deg)	90.00
b(deg)	114.221(3)
g(deg)	90.00
V(Å^3)	4550.0(6)
Z	8
d(calc) gcm^{-3}	1.409
R(int)	0.076
μ, mm^{-1}	1.337
Total data	49346
$>2\sigma(F_O^2)$	1984
R ($>2\sigma$)	0.0411
R_w	0.0825
GOF	1.029

Compound	**2.13**
Empirical Formula	$C_{46}H_{70}N_2Sb$
Formula weight	894.54
Crystal system	Monoclinic
Space group	P 1 21 1
a(Å)	9.2063(10)
b(Å)	28.698(3)
c(Å)	9.4444(11)
a(deg)	90.00
b(deg)	119.062(2)
g(deg)	90.00

V(Å^3)	2181.1(4)
Z	2
d(calc) gcm^{-3}	1.362
R(int)	0.0378
μ, mm^{-1}	1.270
Total data	10284
>2σ(F$_O^2$)	924
R (>2σ)	0.0565
R$_w$	0.0843
GOF	1.022

4) Computational Details

For **2.1**–**2.8**: Calculations were performed with the Gaussian 09 program.[45] To reduce the computational cost, 2,6-dibenzhydryl-4-methylphenyl groups were replaced by 2,6-diisopropylphenyl groups. Geometry optimizations were performed with the M06-2X functional.[46] The 6-31G(d) basis set was used for all the atoms except Au and Fe. The LANL2DZ basis set was applied for Au and Fe. Frequency calculations at the same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum) and provide frontier molecular orbitals (HOMO). Natural bond orbital (NBO) calculations were carried out at the M06-2X/6-311+G(2d,p)//M06-2X/6-31G(d) or M06-2X/6-311+G(2d,p)+SDD//M06-2X/6-31G(d)+LANL2DZ level.

For **2.11**–**2.13**: The DFT calculations were performed with the Gaussian 09 program package[45] with the M05-2X functional.[47] For geometry optimizations and frequency calculations, to verify stationary points, def2-SVP basis sets have been applied while def2-TZVP basis sets were used for single-point calculations.[48] For Sb quasi-relativistic pseudopotentials were employed.[49] For the calculation of LMOs the 2,6-diisopropylphenyl groups were replaced by a hydrogen atom.

The Cartesian coordinates are as follows:

2.1

7	-1.097605	-0.004620	0.631321
6	3.157341	-1.108320	0.097451
6	-2.736480	-3.438523	1.179121
1	-2.672155	-2.883111	2.120419
1	-2.147165	-4.355842	1.278893
1	-3.783565	-3.724166	1.027569
6	-2.224903	-2.598308	0.002486
1	-1.178633	-2.343146	0.197241
6	-3.019004	-1.308420	-0.104850
6	-2.463923	-0.061316	0.209517
7	1.069554	0.017651	0.657370
6	2.427568	0.081738	0.215682
6	2.963410	1.339331	-0.097073
6	4.297220	1.387646	-0.502610
1	4.746496	2.347306	-0.744348
6	5.054081	0.225882	-0.606166
1	6.090641	0.282829	-0.924916
6	-2.259418	-3.396225	-1.304413
1	-1.631206	-4.288360	-1.214466
1	-1.879758	-2.793431	-2.134024
1	-3.275431	-3.727506	-1.546414
6	-4.357808	-1.338463	-0.500366
1	-4.818550	-2.291467	-0.746215
6	-5.105007	-0.170687	-0.576540
1	-6.145095	-0.212505	-0.885987

6	-3.194870	1.136849	0.144476
6	-0.698678	0.082598	1.964716
6	0.648542	0.103694	1.977948
6	4.487539	-1.008850	-0.313780
1	5.084043	-1.912374	-0.409787
6	2.141346	2.612957	-0.002587
1	1.111152	2.338825	0.250761
6	2.674750	3.522160	1.110617
1	2.666518	3.011543	2.079178
1	2.062030	4.425942	1.192077
1	3.705178	3.831619	0.902768
6	2.098350	3.344705	-1.347986
1	3.095278	3.686637	-1.648101
1	1.451467	4.225606	-1.276761
1	1.704834	2.685753	-2.127366
6	2.542911	-2.463819	0.396831
1	1.489326	-2.309576	0.653310
6	3.230837	-3.123009	1.597809
1	4.288121	-3.317286	1.385896
1	2.754803	-4.080654	1.832130
1	3.178800	-2.485542	2.486373
6	2.584728	-3.372364	-0.836695
1	2.071330	-2.898166	-1.677720
1	2.091084	-4.325438	-0.618986
1	3.616637	-3.590984	-1.133698
6	-3.516423	3.504229	1.022793
1	-4.232809	3.844094	0.267423
1	-2.965049	4.385947	1.362991
1	-4.078875	3.100877	1.870779
6	-4.528801	1.054058	-0.255051
1	-5.127275	1.957391	-0.315450
6	-2.539789	2.475563	0.447290
1	-1.758887	2.308073	1.198298
6	-1.860340	3.031659	-0.813026
1	-1.112878	2.338764	-1.213855
1	-1.367853	3.984694	-0.588305
1	-2.607945	3.209339	-1.594644
1	1.358580	0.170913	2.787013
1	-1.425688	0.123232	2.760527
6	-0.001687	-0.058904	-0.196836
15	0.152440	-0.223047	-1.946714
1	-1.256701	-0.200514	-2.125283

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7	1.095348	-0.100661	0.639340
6	-2.915205	1.331260	-0.126910
6	3.343109	3.447575	1.212326
1	3.857972	2.974038	2.052843
1	2.762646	4.291708	1.594663
1	4.098317	3.856539	0.534237
6	2.413011	2.465265	0.493542
1	1.593387	2.231871	1.184550
6	3.112048	1.166493	0.120464
6	2.468498	-0.076965	0.182636
7	-1.064023	-0.049240	0.644281
6	-2.422884	0.051252	0.162355
6	-3.157233	-1.131921	-0.000767
6	-4.468871	-0.995712	-0.455247
1	-5.082470	-1.881143	-0.589614
6	-5.001101	0.257891	-0.738713
1	-6.024636	0.339798	-1.090142
6	1.800605	3.122521	-0.751842
1	1.294779	4.054642	-0.479896
1	1.065911	2.473362	-1.243154
1	2.579843	3.358345	-1.484203
6	4.428729	1.164843	-0.344839
1	4.971880	2.101475	-0.414448
6	5.053929	-0.019065	-0.717085
1	6.078256	0.004002	-1.074898
6	3.064221	-1.293989	-0.178902
6	0.693836	-0.084878	1.961506
6	-0.664215	-0.050200	1.964349
6	-4.233379	1.405306	-0.581240
1	-4.663482	2.375874	-0.810071
6	-2.581692	-2.498008	0.332771
1	-1.488380	-2.409381	0.387197
6	-3.082182	-2.961319	1.708059
1	-2.815508	-2.249958	2.496247
1	-2.652608	-3.934325	1.963908
1	-4.172556	-3.060504	1.703470
6	-2.903477	-3.542805	-0.740583
1	-3.972869	-3.772201	-0.769243
1	-2.376901	-4.475746	-0.520608
1	-2.604721	-3.204920	-1.737769
6	-2.094246	2.597037	0.058714
1	-1.060674	2.317720	0.302643
6	-2.640052	3.416530	1.235354
1	-3.669600	3.734443	1.041010
1	-2.033223	4.313996	1.387921
1	-2.637913	2.835768	2.163039
6	-2.050056	3.435027	-1.223891
1	-1.660054	2.856813	-2.067557
1	-1.406820	4.307927	-1.076693
1	-3.045090	3.802029	-1.494126
6	2.598359	-3.215005	1.354174
1	3.668606	-3.402009	1.489175
1	2.068096	-4.164746	1.471445
1	2.272279	-2.540270	2.152364
6	4.381718	-1.233945	-0.633378
1	4.889665	-2.146848	-0.925852
6	2.334296	-2.619676	-0.036672
1	1.255672	-2.430360	-0.119302
6	2.701721	-3.623433	-1.132492
1	2.600945	-3.187480	-2.131311
1	2.044900	-4.495396	-1.070012
1	3.728262	-3.985109	-1.020291
1	-1.382162	-0.017231	2.769190
1	1.415704	-0.085879	2.763898

6	0.012201	-0.088216	-0.154028
15	-0.083215	-0.028564	-1.993182
1	-0.807828	-1.242205	-2.080213
1	1.189206	-0.622045	-2.163980

2.6

7	-1.687911	0.483061	0.921933
6	2.824010	0.904939	1.298018
6	-3.279374	-2.351848	3.139645
1	-3.452497	-1.400816	3.654238
1	-2.657976	-2.982123	3.782880
1	-4.248904	-2.847221	3.018272
6	-2.591756	-2.138723	1.786253
1	-1.624153	-1.663977	1.970706
6	-3.414852	-1.236869	0.886369
6	-2.949793	-0.002461	0.422135
7	0.379756	1.089487	1.117231
6	1.700148	1.540258	0.750702
6	1.789704	2.651541	-0.103666
6	3.067526	3.083326	-0.460759
1	3.172889	3.934913	-1.126814
6	4.200732	2.451988	0.035951
1	5.185957	2.799001	-0.259125
6	-2.312477	-3.475218	1.088327
1	-1.656656	-4.092142	1.709051
1	-1.816978	-3.316681	0.124847
1	-3.240883	-4.029711	0.911750
6	-4.679279	-1.650237	0.454954
1	-5.070597	-2.603832	0.797751
6	-5.427424	-0.869149	-0.411572
1	-6.405558	-1.207339	-0.739096
6	-3.670612	0.803165	-0.479337
6	-1.555037	1.084343	2.166313
6	-0.266361	1.470679	2.282680
6	4.077647	1.386327	0.917919
1	4.969578	0.914250	1.318427
6	0.573555	3.448305	-0.548336
1	-0.330811	2.894516	-0.278315
6	0.529088	4.781138	0.212167
1	0.506075	4.619143	1.294945
1	-0.361619	5.352730	-0.069355
1	1.410253	5.389408	-0.019061
6	0.538494	3.675954	-2.061422
1	1.371766	4.306603	-2.389567
1	-0.390074	4.187866	-2.338156
1	0.584887	2.725214	-2.599293
6	2.713510	-0.199419	2.331982
1	1.692701	-0.588984	2.310731
6	2.978290	0.372509	3.732928
1	3.995575	0.774677	3.796113
1	2.873408	-0.410692	4.490412
1	2.287112	1.184298	3.982524
6	3.665527	-1.367639	2.056608
1	3.576082	-1.714315	1.023756
1	3.427694	-2.201905	2.724002
1	4.708119	-1.085090	2.239985
6	-3.310230	3.250358	0.024177
1	-4.378193	3.410925	0.209427
1	-2.887288	4.184655	-0.361733
1	-2.825861	3.033797	0.981306
6	-4.921604	0.340162	-0.882216
1	-5.510223	0.924928	-1.580498
6	-3.108616	2.120159	-0.994648
1	-2.031962	1.981616	-1.146061
6	-3.683123	2.526433	-2.352627
1	-3.597334	1.715013	-3.081459
1	-3.131712	3.389475	-2.737553
1	-4.736154	2.819251	-2.278471
1	0.258761	1.987373	3.069590
1	-2.396992	1.171274	2.834838
6	-0.491034	0.466305	0.279366
15	-0.121801	-0.084468	-1.407027
1	-1.402289	-0.679451	-1.536499
26	1.455113	-1.941793	-1.326975
6	2.674874	-3.283110	-1.321802
6	0.474534	-2.659452	-2.669106
6	0.938830	-2.304939	0.343907
6	2.713801	-0.691521	-1.765947
8	3.467088	0.126840	-2.046479
8	0.586880	-2.509190	1.426609
8	3.448386	-4.125934	-1.303627
8	-0.190752	-3.103552	-3.492210

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7	-1.303711	1.569955	1.144977
6	1.746771	-1.610530	1.884459
6	-4.709430	0.916447	2.288457
1	-4.061903	1.513417	2.938810
1	-5.023757	0.027407	2.843104
1	-5.600909	1.513216	2.065840
6	-4.004950	0.505114	0.988147
1	-3.113081	-0.078426	1.251330
6	-3.557018	1.731190	0.211480
6	-2.250549	2.226638	0.274642
7	0.408335	0.446213	1.835980
6	1.695813	-0.214056	1.821844
6	2.824816	0.610707	1.692578
6	4.061369	-0.027864	1.611687
1	4.960594	0.564443	1.471325
6	4.153736	-1.413863	1.654291
1	5.123546	-1.889090	1.552548
6	-4.916801	-0.403161	0.156066
1	-5.037392	-1.367794	0.655338
1	-4.492438	-0.602751	-0.832563
1	-5.909242	0.042879	0.026642
6	-4.452889	2.429497	-0.603645
1	-5.478255	2.083097	-0.681914
6	-4.044582	3.542675	-1.325022

1	-4.756259	4.066695	-1.955280
6	-1.789191	3.331008	-0.463581
6	-1.186385	1.808546	2.500784
6	-0.116028	1.097000	2.934415
6	3.013160	-2.193713	1.799514
1	3.101902	-3.274971	1.829223
6	2.749483	2.129819	1.628216
1	1.700076	2.441384	1.700989
6	3.486606	2.749799	2.822477
1	3.097332	2.370039	3.772661
1	3.375957	3.838833	2.813222
1	4.556329	2.520154	2.782859
6	3.295931	2.678598	0.303946
1	4.318208	2.335852	0.115461
1	3.296713	3.774576	0.327447
1	2.691119	2.349992	-0.548066
6	0.506642	-2.465208	2.072857
1	-0.374138	-1.867095	1.807608
6	0.360854	-2.860558	3.548588
1	1.224393	-3.451272	3.873293
6	0.508671	-3.705373	1.172933
1	0.749432	-3.445878	0.135808
1	-0.480281	-4.174036	1.181194
1	1.240487	-4.444419	1.516934
6	-0.170722	4.811220	0.766179
1	-0.782426	5.702610	0.589540
1	0.876684	5.122853	0.841042
1	-0.467500	4.381483	1.728590
6	-2.724785	3.982564	-1.264957
1	-2.420495	4.839760	-1.856041
6	-0.345582	3.808471	-0.382889
1	0.294694	2.944393	-0.166085
6	0.163874	4.401123	-1.698401
1	-0.010783	3.721443	-2.538216
1	1.240486	4.580628	-1.624101
1	-0.313699	5.360299	-1.923725
1	0.340931	1.002319	3.906776
1	-1.866914	2.470016	3.012760
6	-0.329050	0.730123	0.746312
15	-0.162856	-0.032429	-0.923824
1	-0.772566	1.031695	-1.616464
1	-0.541421	-3.463134	3.690646
1	0.294159	-1.979139	4.195821
79	-1.644211	-1.779919	-0.722224
79	2.059909	-0.230315	-1.442975
17	-3.123205	-3.567242	-0.279381
17	4.362743	-0.371405	-1.937754

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7	1.124189	-0.049771	-0.691155
6	-3.107492	-1.190228	-0.147177
6	2.939331	-3.347892	-1.412730
1	2.766605	-2.777087	-2.331183
1	2.413293	-4.303699	-1.497538
1	4.012718	-3.556971	-1.344301
6	2.456006	-2.580394	-0.176333
1	1.380255	-2.401216	-0.286231
6	3.163336	-1.240904	-0.071440
6	2.506482	-0.022334	-0.280446
7	-1.031823	-0.018504	-0.694233
6	-2.417995	0.023733	-0.274218
6	-2.996550	1.281612	-0.046889
6	-4.334069	1.294996	0.348190
1	-4.819623	2.243698	0.550406
6	-5.046385	0.111374	0.499588
1	-6.084055	0.145103	0.817526
6	2.640059	-3.408207	1.099883
1	2.054758	-4.329986	1.031655
1	2.292300	-2.859364	1.979682
1	3.689780	-3.684515	1.248007
6	4.519263	-1.178584	0.254892
1	5.066984	-2.101603	0.421581
6	5.170514	0.042777	0.378241
1	6.225627	0.067987	0.632854
6	3.118278	1.228984	-0.128656
6	0.728473	-0.039226	-2.014920
6	-0.625738	-0.019436	-2.014879
6	-4.443423	-1.114566	0.248319
1	-5.013717	-2.029236	0.371673
6	-2.232284	2.574570	-0.280217
1	-1.176507	2.386304	-0.056299
6	-2.358096	3.003855	-1.750342
1	-1.979041	2.244615	-2.440772
1	-1.797264	3.928172	-1.924691
1	-3.408257	3.191024	-2.000532
6	-2.681787	3.718793	0.630034
1	-3.675990	4.085743	0.351107
1	-1.984266	4.555785	0.527996
1	-2.690493	3.409540	1.676911
6	-2.465848	-2.524731	-0.489572
1	-1.386073	-2.433662	-0.325934
6	-2.717512	-2.860499	-1.967716
1	-3.793074	-2.949602	-2.156669
6	-2.955426	-3.674964	0.392653
1	-2.854807	-3.427787	1.451115
1	-2.354778	-4.566962	0.189788
1	-3.999219	-3.929407	0.177435
6	2.739708	3.198892	-1.635522
1	3.808233	3.440546	-1.655412
1	2.178628	4.129099	-1.769646
1	2.527615	2.544633	-2.487642
6	4.475116	1.232814	0.197300
1	4.989063	2.181472	0.319538
6	2.361818	2.534254	-0.305812
1	1.288395	2.313519	-0.330807
6	2.592003	3.486642	0.871889
1	2.348238	3.004055	1.822092
1	1.947383	4.364693	0.767416

1	3.629539	3.836163	0.907984
1	-1.342122	-0.001987	-2.820269
1	1.450619	-0.046167	-2.815922
6	0.044753	-0.040052	0.116613
15	0.048858	-0.092441	1.961952
1	1.456423	-0.132552	2.030639
1	-2.246205	-3.814274	-2.226299
1	-2.323200	-2.094284	-2.642123
5	-0.656760	-1.856619	2.491322
1	-0.196773	-1.986949	3.603007
1	-1.857511	-1.723522	2.483842
5	-0.570335	1.645549	2.653769
1	-0.146224	1.618819	3.786674
1	-0.068631	2.515121	1.970349
1	-0.232131	-2.671308	1.696163
1	-1.775667	1.588252	2.595405

2.10

6	1.01993500	1.99674000	1.80037700
6	0.51897100	0.19960400	0.31206300
6	-0.37294700	1.42904500	2.09025300
1	0.92807800	2.97510100	1.30883000
1	1.58242400	2.13757500	2.72918400
6	-1.89036500	0.38496300	0.17280000
6	-2.62200500	-0.79017500	0.44365100
6	-2.33190200	1.33245500	-0.78265200
6	-3.76427200	-1.03845900	-0.32509700
6	-3.47712000	1.02417300	-1.52021500
6	-4.17966500	-0.15583100	-1.31137000
1	-4.33381700	-1.94708800	-0.13953300
1	-3.82635000	1.72991000	-2.27203200
1	-5.06304500	-0.37874600	-1.90793100
7	-0.60210800	0.63147400	0.81123600
6	-0.32891800	0.44651100	3.26584300
1	0.05427200	0.98075400	4.14431000
1	-1.32824500	0.07112700	3.50729100
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6	-1.43759000	2.47994100	2.34874700
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1	-1.38448700	3.31140400	1.64262100
6	-2.29365900	-1.75512900	1.56899600
1	-1.28482500	-1.53967700	1.92919900
6	-1.72151000	2.71619500	-0.97543700
1	-0.82490500	2.78576900	-0.34850400
6	-2.29642100	-3.22197100	1.12546100
1	-1.90824700	-3.84661400	1.93904500
1	-3.30913000	-3.57009000	0.88251300
1	-1.64979000	-3.37819200	0.25495000
6	-3.29349900	-1.55337900	2.71823900
1	-2.99934100	-2.15791800	3.58644400
1	-3.35789100	-0.50233600	3.02848800
1	-4.30021700	-1.86681300	2.41008800
6	-2.73526600	3.78137000	-0.51760100
1	-3.55148100	3.85732000	-1.24786300
1	-3.18323100	3.54902900	0.45443600
1	-2.25065500	4.76525500	-0.45844700
6	-1.30144000	3.03312400	-2.41476500
1	-2.15848400	2.96926500	-3.09809200
1	-0.92074000	4.06241600	-2.45858500
1	-0.52861700	2.34937200	-2.77122800
51	0.50974700	-1.54799800	-1.07764400
17	0.41163400	0.08404200	-2.96692600
17	2.86109100	-1.75417700	-1.51039700
17	1.02285900	-2.50881000	1.29969600
6	1.70187400	0.98091500	0.84643700
6	2.81102300	0.16021900	1.54008800
6	2.29585800	1.69437800	-0.40135400
6	4.03295600	1.01944800	1.86942100
1	3.10822900	-0.66171300	0.88029500
1	2.41220600	-0.30616700	2.44737300
6	3.49951700	2.55878600	-0.02980400
1	2.60713800	0.93512500	-1.13021600
1	1.51391800	2.29505500	-0.88756000
6	4.58583300	1.71030700	0.62552500
1	4.79788800	0.37674100	2.32442800
1	3.77798600	1.78175800	2.62265200
1	3.87930600	3.04430600	-0.93823400
1	3.19442700	3.36430400	0.65725700
1	5.45725800	2.32730500	0.88197400
1	4.92437800	0.94631400	-0.09067300

2.11a

6	1.45084200	0.99634600	2.15389900
6	0.64019100	-0.07142900	0.17045000
6	-0.02855100	0.62972100	2.30678500
1	1.55292600	2.08408700	2.03722200
1	2.01599300	0.70037900	3.04375000
6	-1.72023600	0.54602300	0.30434900
6	-2.70717900	-0.45875200	0.33252900
6	-1.97625500	1.81767200	-0.26051800
6	-3.94176700	-0.17794200	-0.26356800
6	-3.22561300	2.03554900	-0.84606900
6	-4.20177200	1.04797600	-0.85805600
1	-4.71115400	-0.94831000	-0.25929000
1	-3.43326300	3.00289900	-1.30040600
1	-5.16756700	1.23785400	-1.32410200
7	-0.38847000	0.33260500	0.85722800
6	-0.18776700	-0.65748300	3.12098100
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1	-1.24269100	-0.90033200	3.27868200
1	0.29616900	-1.50636600	2.62166100
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1	-1.94514300	1.48739200	2.85799700
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1	-3.87758100	-3.01949300	-0.24936300
1	-2.22395300	-2.86708800	-0.89622200
6	-3.44932000	-1.92749800	2.21936100
1	-3.23262800	-2.85399600	2.76728300
1	-3.32722300	-1.07890300	2.90505200
1	-4.50456400	-1.95295800	1.91561600
6	-1.60972500	4.21034900	0.44620800
1	-2.39148200	4.65660800	-0.18153400
1	-2.06228300	3.96380400	1.41379100
1	-0.83851200	4.97617600	0.60266400
6	-0.54697800	3.36885600	-1.66118700
1	-1.40415700	3.71668200	-2.25360500
1	0.17933000	4.19146300	-1.60816100
1	-0.08291900	2.52786300	-2.18511200
51	0.46055200	-1.29890300	-1.69455500
17	1.23168900	0.63041900	-3.13250400
17	0.56991800	-3.02588100	0.29951000
6	1.94107300	0.27666600	0.87159400
6	2.87759200	-0.91732900	1.14860500
6	2.68241000	1.26234400	-0.07132200
6	4.22573900	-0.47005800	1.71563600
1	3.03804400	-1.45589400	0.20367800
1	2.39049300	-1.63348100	1.81797000
6	4.00352200	1.73045100	0.53667200
1	2.87847000	0.76146500	-1.02790200
1	2.03256300	2.11719300	-0.30634800
6	4.92069600	0.54032900	0.80612400
1	4.85716500	-1.35654400	1.85969800
1	4.08641800	-0.02362400	2.71237300
1	4.48048800	2.43897100	-0.15305200
1	3.82170700	2.27620400	1.47591200
1	5.86671900	0.87358800	1.25307000
1	5.16816100	0.05627500	-0.15095800

2.11b

6	1.24467800	1.80967200	1.70647600
6	0.57524200	0.22042300	0.06375300
6	-0.19808800	1.35651600	1.99923100
1	1.22342900	2.82143200	1.27697100
1	1.83595500	1.85615200	2.62794600
6	-1.82784500	0.63740400	0.09744400
6	-2.77484900	-0.35994200	0.41597300
6	-2.09899600	1.59922500	-0.90721600
6	-4.00061600	-0.35556600	-0.26113900
6	-3.33093300	1.55245900	-1.56140600
6	-4.28072400	0.58796300	-1.23935400
1	-4.74258800	-1.11573900	-0.02066200
1	-3.55222000	2.28488200	-2.33670600
1	-5.23828600	0.56982600	-1.75815500
7	-0.54115700	0.66380800	0.72751300
6	-0.21959000	0.38187600	3.18447700
1	0.23286600	0.86613500	4.05966100
1	-1.24235100	0.09658500	3.44760700
1	0.34872000	-0.52709600	2.95466100
6	-1.14000500	2.52193500	2.27692600
1	-2.17151700	2.17000600	2.40912800
1	-0.82785800	3.02383200	3.20147500
1	-1.12272600	3.25421900	1.46204100
6	-2.52269600	-1.43657100	1.45730000
1	-1.46845500	-1.37597600	1.75076500
6	-1.09618100	2.66979900	-1.30805900
1	-0.27998700	2.64912900	-0.57913400
6	-2.76611600	-2.84832100	0.90902000
1	-2.45642400	-3.59199600	1.65400800
1	-3.82837600	-3.01334700	0.68582800
1	-2.18802800	-3.03936500	-0.00262200
6	-3.40209400	-1.20354400	2.69423400
1	-3.12786800	-1.90035400	3.49741900
1	-3.31227000	-0.17824700	3.07352100
1	-4.45919300	-1.37071700	2.44630700
6	-1.71359000	4.07346400	-1.28707500
1	-2.45277000	4.19883400	-2.08884300
1	-2.21377700	4.28111600	-0.33280900
1	-0.93141400	4.82819200	-1.44203100
6	-0.49142300	2.37412800	-2.68626900
1	-1.27340400	2.34630300	-3.45734800
1	0.23188000	3.15409000	-2.95977000
1	0.03320300	1.41052300	-2.69131300
51	0.28063800	-1.46055800	-1.16448400
17	2.45474800	-1.51907800	-2.18211000
17	0.77286600	-3.18556800	0.51405800
6	1.83610300	0.82119100	0.66325300
6	2.76163900	-0.24822500	1.28939400
6	2.63579200	1.59394700	-0.41178500
6	4.06736300	0.33823300	1.82934100
1	3.00210600	-0.98508800	0.51003000
1	2.22965900	-0.79743800	2.07540100
6	3.91899900	2.20347400	0.15474300
1	2.89514700	0.89999100	-1.22109600
1	1.99310700	2.37333200	-0.84588700
6	4.81438500	1.11641000	0.74789000
1	4.69402300	-0.47617600	2.21686200
1	3.86301000	1.00611400	2.68066100
1	4.44897700	2.74657300	-0.63950700
1	3.67373200	2.94294200	0.93380400
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1	5.11132400	0.42267700	-0.05384600

2.12

51	-0.28579800	-1.81580500	-0.73940300
17	-2.62137600	-2.54800600	-0.92550300
6	-1.90471500	0.81624800	0.39543500

6	0.08218300	2.05974200	1.21712500
7	0.43663500	0.81643700	0.46330600
6	-2.72921300	0.09298700	1.48595100
1	-2.88739500	-0.94119800	1.15415800
1	-2.15434800	0.04945900	2.42083300
6	-0.61324000	0.06909500	0.10462500
6	-4.08908700	0.75434000	1.72131900
1	-4.64807000	0.16741600	2.46239200
1	-3.95943300	1.75954700	2.15235600
6	0.24262800	1.86434200	2.72796400
1	-0.34045300	1.00966300	3.08823100
1	-0.11809100	2.76626800	3.23852900
1	1.29216200	1.71752300	2.99937900
6	3.49010900	0.35865000	-1.60686200
1	3.86222900	0.64631800	-2.58923800
6	-1.39804700	2.21450800	0.83705000
1	-1.48505600	2.91515200	-0.00461400
1	-1.97576000	2.62656600	1.67184400
6	3.80001600	-0.82307300	0.46317700
1	4.41542400	-1.45687200	1.10001800
6	2.09201400	-0.88910600	2.29378500
1	1.06260300	-0.54958000	2.44422900
6	0.93520300	3.24702400	0.78574000
1	2.00219700	3.04012400	0.94460400
1	0.66100300	4.11919200	1.39232000
1	0.77363800	3.49840800	-0.26635200
6	2.53891000	-0.42062800	0.91835200
6	1.76273600	0.41239300	0.08038900
6	2.09267200	-2.41835400	2.41892300
1	1.45191200	-2.87593100	1.65751200
1	1.71428200	-2.70669200	3.40856100
1	3.10723700	-2.82599800	2.31924100
6	2.22409400	0.79032000	-1.20532600
6	4.27627300	-0.43740000	-0.78211800
1	5.25990300	-0.76496200	-1.11591200
6	1.41730400	1.64222600	-2.17533200
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6	2.99056900	-0.28783100	3.38570700
1	3.99074500	-0.73970200	3.34635400
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1	3.11773100	0.79545600	3.27184600
6	2.16498500	2.93651400	-2.52915800
1	2.51019600	3.47153600	-1.63691900
1	1.51155700	3.60308500	-3.10761400
1	3.04485100	2.71796100	-3.14846800
6	1.07863700	0.87353900	-3.45986300
1	1.99231300	0.60228200	-4.00579700
1	0.46695500	1.50317800	-4.11990200
1	0.52222700	-0.04235100	-3.23387400
6	-2.74706600	0.93600500	-0.89442000
1	-2.16021300	1.47651200	-1.65183600
1	-2.94216900	-0.06889000	-1.28568400
6	-4.88178400	0.86277000	0.41947300
1	-5.85036600	1.34783900	0.60079600
1	-5.08744400	-0.14953900	0.03960000
6	-4.08256000	1.63184700	-0.63182500
1	-4.64739200	1.69887700	-1.57113500
1	-3.91722700	2.66524900	-0.28644700

2.13

51	-1.27739800	0.60000700	0.71710700
51	1.27744300	-0.59999800	0.71711700
6	-2.53353100	-0.68870100	-0.39279900
6	-2.20168300	-1.83686400	-1.33970400
6	-3.55329200	-2.12000600	-2.03295800
6	-4.65150100	-1.54360000	-1.13261700
6	-5.33345800	-2.61456100	-0.28009400
6	-5.73269300	-0.83796700	-1.94622100
7	-3.86604200	-0.58297400	-0.29213400
6	-4.52085500	0.34543300	0.59409400
6	-4.79028700	-0.02995100	1.93240400
6	-5.49917200	0.86527900	2.73852500
6	-5.90595500	2.10511000	2.26303600
6	5.57806400	2.48378800	0.96834400
6	-4.87485200	1.62729100	0.11580900
6	-4.48266300	2.15853500	-1.25664500
6	-5.70009400	2.59946400	-2.08187500
6	-3.51321200	3.34216500	-1.12226100
6	-4.29615400	-1.31947000	2.57506600
6	-3.30428000	-1.01866000	3.70901800
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6	4.52085700	-0.34544100	0.59411500
6	4.79013400	0.02987500	1.93246600
6	5.49895800	-0.86538200	2.73861800
6	5.90586100	-2.10516100	2.26309400
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6	4.87491400	-1.62726800	0.11580600
6	4.48286800	-2.15846600	-1.25670700
6	3.51337200	-3.34206500	-1.12248600
6	5.70039100	-2.59941800	-2.08177700
6	4.29593300	1.31935000	2.57514300
6	3.30402900	1.01854600	3.70907400
6	5.44079600	2.17545200	3.13604600
6	4.65153200	1.54364400	-1.13253800
6	3.55332800	2.12004500	-2.03292100
6	2.20169500	1.83686600	-1.33971100
6	1.69113900	3.04472800	-0.51659600
6	1.29482500	4.22935800	-1.40032300
6	0.26763100	3.81148300	-2.45213400
6	0.78353600	2.63691700	-3.28342900

6	1.13302000	1.45639900	-2.37709400
6	5.73274600	0.83796000	-1.94606000
6	5.33341700	2.61458800	-0.27992000
1	-5.86247600	3.47221100	0.61002700
1	-6.45847100	2.78549500	2.90981900
1	-5.72084700	0.58690000	3.76791900
1	5.86262100	-3.47215500	0.61000300
1	6.45832900	-2.78557100	2.90989300
1	5.72050500	-0.58706100	3.76805600
1	-3.57209000	-1.60363400	-3.00225100
1	-3.72102700	-3.18580700	-2.22305800
1	-5.86781400	-3.30507900	-0.94498000
1	-4.61970300	-3.19307000	0.31491600
1	-6.06637000	-2.15271800	0.38972500
1	-5.30301400	-0.10159300	-2.63197700
1	-6.26748600	-1.58922200	-2.54160300
1	-6.45696700	-0.34038000	-1.28888000
1	-3.95383700	1.36057800	-1.79119700
1	-6.46668300	1.82038700	-2.14928700
1	-6.16524000	3.48907500	-1.63720500
1	-5.38540900	2.86826800	-3.09918200
1	-4.00342500	4.19273100	-0.62930500
1	-2.62997900	3.06087900	-0.53801700
1	-3.18691300	3.67209100	-2.11804500
1	-3.75639400	-1.89063300	1.81261900
1	-2.47447300	-0.40093000	3.35055900
1	-3.80482400	-0.49621500	4.53559200
1	-2.89633300	-1.95943800	4.10278900
1	-5.90380500	-1.68092000	4.00022500
1	-6.23019800	-2.36863200	2.40208900
1	-5.04880100	-3.14075300	3.48312900
1	-1.48819500	-0.59456800	-2.96165800
1	-0.22871100	-1.13898000	-1.84371900
1	-1.66607000	-2.95092900	-3.86364000
1	-0.02320400	-2.32408600	-4.01224400
1	-0.01498300	-4.66329200	-3.09865900
1	0.65630000	-3.50249700	-1.94196400
1	-2.18092300	-4.64926200	-1.90079200
1	-0.88790100	-5.02877300	-0.76649800
1	-0.81094800	-2.71174600	0.05000800
1	-2.44905700	-3.34569800	0.21934100
1	3.95412200	-1.36048200	-1.79127200
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1	2.63026300	-3.06086100	-0.53802200
1	3.18689500	-3.67168700	-2.11831300
1	6.46702400	-1.82037500	-2.14907300
1	6.16545100	-3.48904700	-1.63705300
1	5.38583100	-2.86819300	-3.09913300
1	3.75617500	1.89049900	1.81268900
1	2.47430000	0.40069300	3.35064300
1	3.80456700	0.49624500	4.53573900
1	2.89597300	1.95932700	4.10272700
1	5.90351500	1.68088400	4.00036000
1	6.23000800	2.36847400	2.40218400
1	5.04855400	3.14069300	3.48309200
1	3.72103300	3.18587000	-2.22292100
1	3.57219100	1.60377000	-3.00225300
1	0.81102700	2.71180600	0.05009400
1	2.44916700	3.34574500	0.21930100
1	0.88790200	5.02880000	-0.76647700
1	2.18086900	4.64928600	-1.90082500
1	-0.65631600	3.50247500	-1.94188300
1	0.01490900	4.66329100	-3.09859100
1	0.02309700	2.32408200	-4.01214000
1	1.66596200	2.95097400	-3.86369300
1	1.48818100	0.59458200	-2.96165200
1	0.22872600	1.13901500	-1.84368600
1	6.45708200	0.34052100	-1.28867500
1	5.30310300	0.10145600	-2.63171400
1	6.26746300	1.58918000	-2.54156000
1	4.61961500	3.19300500	0.31513600
1	6.06637800	2.15277500	0.38986800
1	5.86770800	3.30519300	-0.94476200

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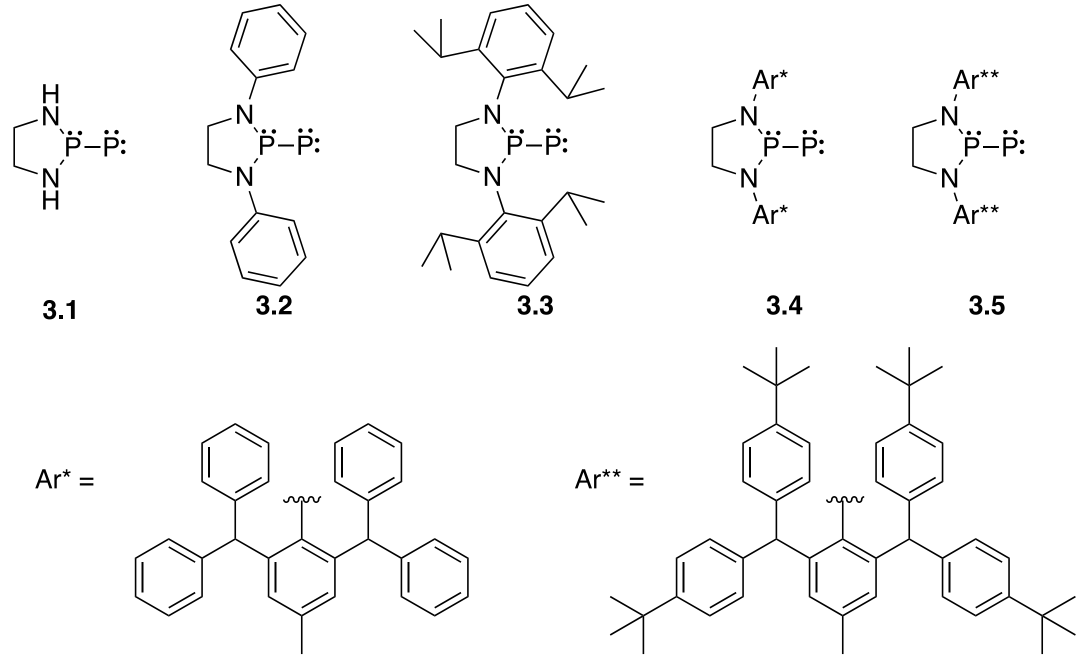
Chapter 3:

A Stable Singlet Phosphinidene

Introduction

In the previous chapter, a carbene-stabilized phosphinidene was explored. So far, phosphinidenes as free entities have never been isolated. This is due to their extreme reactivity arising from the phosphorus atom having two lone pairs and a vacant orbital. They are analogues of carbenes, and as described for carbenes in the introduction, they can exist in the singlet or triplet state. In the triplet state their diradical character makes these species highly unstable. Indeed, triplet phosphinidenes have only been detected in the gas phase by mass spectrometry[1] or in low temperature matrices by EPR, IR, and UV/Vis spectroscopy.[2] Although triplet carbenes are still quite elusive,[3] singlet carbenes with the right set of substituents can be isolated and stored.[4] Our lab also recently reported for the first time that a singlet nitrene could be isolated.[5] In contrast, singlet phosphinidenes have never even been spectroscopically characterized.[6] Singlet phosphinidene intermediates have been postulated based on trapping experiments, but no spectroscopic evidence exists.[7] The problem arises from phosphinidenes' inherit triplet ground state, however theoretical studies have shown that the singlet state can be stabilized with the right substituents.[8]

Nguyen *et al.* concluded from their computational investigation[9] that the implantation of amino groups in the β-position of phosphino-phosphinidenes would stabilize the singlet state by means of lone pair repulsion. From this analysis, the rigid 1,3,2-diazaphospholidine scaffold[10] seems like an ideal candidate to favor the singlet state. We performed calculations at the M06-2X/Def2-SVP level of theory on **3.1** and found that the singlet ground state is 17.4 kcal/mol below the triplet state. Since steric protection will be crucial to isolate such a compound, and bulky substituents at nitrogen of five-membered rings prevent their pyramidalization,[11] which maximizes the interaction between the nitrogen and phosphorus lone pair, we also studied the singlet–triplet gap of **3.2-3.4** (Figure 3.1). The singlet–triplet gap increases from 8.2 to 17.2 and 23.5 kcal/mol when going from the phenyl groups of **3.2**, to Dipp of **3.3**, and the bulky 2,6-dibenzhydryl-4-methylphenyl groups (Ar*)[12] of **3.4**, respectively.

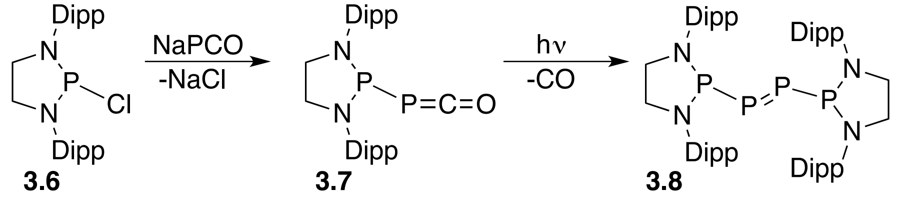


3.1 **3.2** **3.3** **3.4** **3.5**

Figure 3.1: Depiction of phosphino-phosphinidenes **3.1-3.5**.

A) Evidence for a transient phosphinidene

The chlorodiazaphospholidine **3.6** has been studied in detail showing that the P–Cl bond can be transformed into other moieties,[10] making it a suitable precursor to generate the desired phosphinidene. Transient carbenes and nitrenes are typically made from the corresponding diazo and azide derivatives, but this type of terminal fragment does not exist with phosphorus (i.e. –PN_2).[13] However, there are a few examples using ketenes[14] and isocyanates[15] as precursors, and the terminal –PCO fragment is known. Indeed, the chemistry of the phosphaethynolate anion (PCO^{-})[16] has gained interest in recent years,[17] thanks to the novel synthetic methods developed to generate the compound in a large scale and convenient fashion.[18] It has been used to install simple PCO units into various frameworks,[19] it undergoes cycloaddition reactions forming unusual P-containing heterocycles,[20] and reactivity as a P transfer agent has been documented.[21] Thus, utilizing the PCO^{-} anion would provide direct access to the desired precursor. Reacting chlorodiazaphospholidine **3.6** with NaPCO led to phosphaketene **3.7** (Scheme 3.1). The difference in electronic environments between the two P atoms is apparent by the large difference in their ^{31}P NMR chemical shifts (168 ppm for the cyclic P, and –245 ppm for P*P*CO). The peaks appear as an AX system (J_{PP} = of 252 Hz). Single crystals suitable for an X-ray diffraction were grown from pentane at room temperature. The structure reveals an exceptionally long PP bond distance of 2.3781(8) Å (Figure 3.2).



Scheme 3.1: Synthesis of phosphaketene **3.7** and its UV irradiation induced CO elimination to generate diphosphene **3.8**.

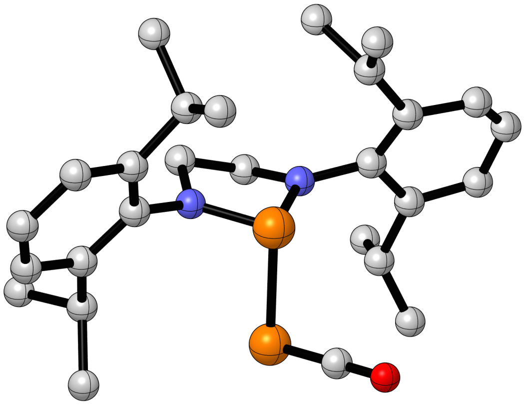


Figure 3.2: Molecular view of **3.7** in the solid state with hydrogen atoms omitted for clarity.

In order to generate the desired phosphino-phosphinidene, the photolytic cleavage of the PC bond of **3.7** was attempted. **3.7** was dissolved in pentane and irradiated with a medium pressure mercury UV lamp (200 – 400 nm) for three hours at room temperature (Scheme 3.1). Purple crystals formed from the solution and after workup the crystals were isolated in 61% yield. The ^{31}P NMR spectrum of the crystals displayed two triplets at 675 and 137 ppm (J_{PP} = 75 Hz). This is not what the expected phosphino-phosphinidene spectrum should appear as; instead it is indicative of a diphosphene unit composed of four phosphorus nuclei. The crystals were subjected to an X-ray diffraction study and the solid-state structure revealed **3.8**, which is the dimer of the desired phosphino-phosphinidene (Figure 3.3). The central PP bond length (2.024(1) Å) falls in the range for PP double bonds,[22] and the outer PP bond lengths (2.271(1) Å) are typical for PP single bonds.

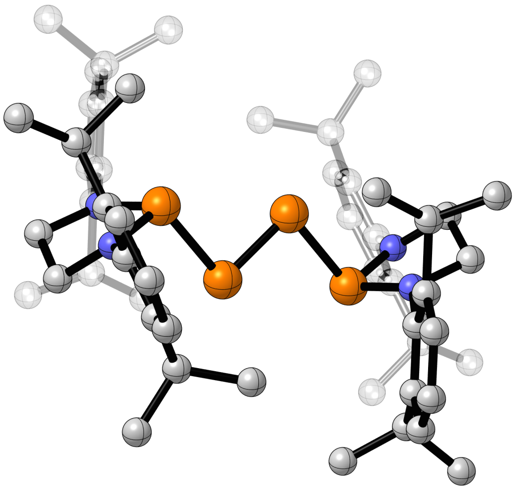
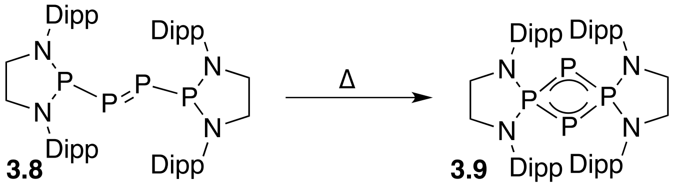


Figure 3.3: Molecular view of **3.8** in the solid state with hydrogen atoms omitted for clarity.

An interesting aspect of **3.8** is its thermal instability. Heating a pentane solution of **3.8** at 40 ºC overnight resulted in a new product (Scheme 3.2). After work-up, yellow crystals of **3.9** were isolated in 63% yield. The solid-state structure revealed that the terminal dimer had rearranged into what could be considered a head to tail dimer (Figure 3.4). As observed previously for these types of systems,[7c] the ^{31}P NMR spectrum displays an A_2B_2 spin system with a set of 14 peaks.



Scheme 3.2: Thermal rearrangement of **3.8** into **3.9**.

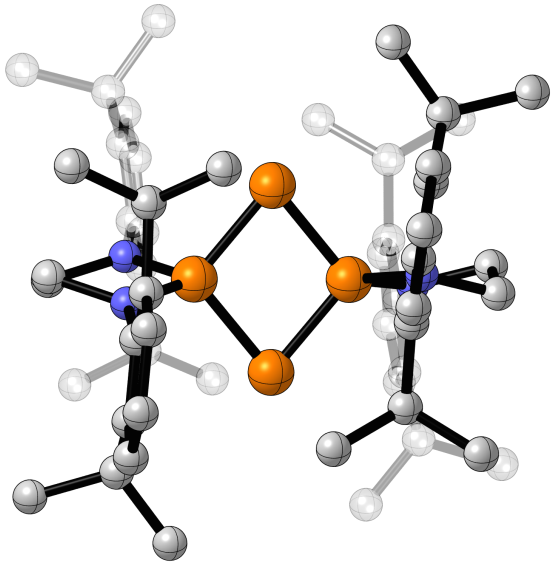
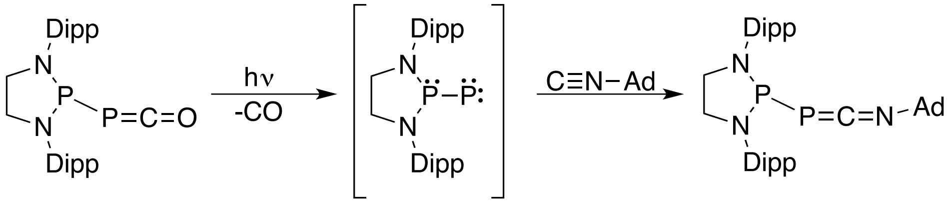


Figure 3.4: Molecular view of **3.9** in the solid state with hydrogen atoms and solvent molecules omitted for clarity.

Although **3.8** appears to result from phosphinidene dimerization, recent calculations performed on a phosphaketene substituted by a diazaphosphole[23] (the unsaturated analogue of **3.7**) predicted that the dissociation energy into the phosphino-phosphinidene and CO has a high-energy activation barrier.[24] To check for the transient formation of **3.3**, the irradiation of **3.7** was performed in the presence of an isocyanide (Scheme 3.3), which have been shown as effective trapping agent for carbenes[25] and nitrenes.[5] After work-up, phosphinidene-isocyanide[26] adduct **3.10** was isolated in 52% yield. The solid-state structure revealed the expected coupling product (Figure 3.5). Thus, **3.3** is the likely intermediate and the Dipp groups are not sterically bulky enough to kinetically prevent its dimerization.



3.7 **3.3** **3.10**

Scheme 3.3: Irradiation of **3.7** in the presence of 1-adamantyl isonitrile affording phosphinidene-isonitrile coupling product **3.10**.

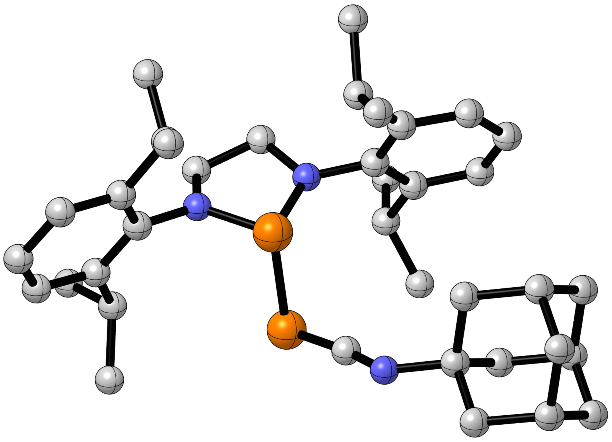
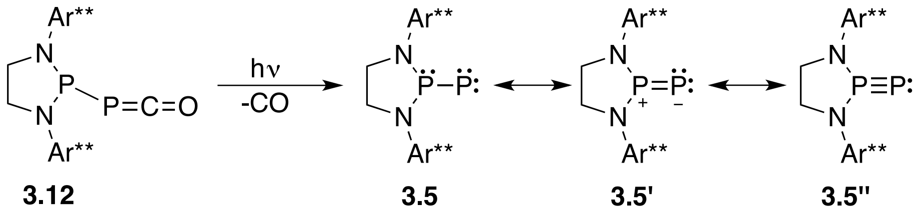


Figure 3.5: Molecular view of **3.10** in the solid state with hydrogen atoms omitted for clarity.

B) Synthesis of a stable phosphino-phosphinidene

In the previous chapter, we demonstrated that bulky ligands can allow for the isolation of species where smaller versions fail. Based on the dimerization result of **3.8**, we sought to create a sterically encumbering diazaphospholidine. The Dipp groups of **3.7** where replaced by the 2,6-bis[(4-*tert*-butylphenyl)methyl]-4-methylphenyl substituents (Ar**) that Straub and co-workers[27] have utilized to isolate reactive fragments.[28] Chlorodiazaphospholidine **3.11** and the ensuing phosphaketene **3.12** were prepared following a similar procedure to that of the Dipp analogue. Phosphaketene **3.12** has similar ^{31}P NMR resonances (173 and –241 ppm) as **3.7**. Irradiating **3.12** for 3 hours afforded a new compound as observed by ^{31}P NMR spectroscopy (Scheme 3.4). The spectrum shows two resonances at 80 and –200 ppm (Figure 3.6), vastly different from dimer **3.8**. The high field signal for the terminal phosphorous and the enormous PP coupling constant (J_{PP} = 884 Hz) are indicative of a negatively charged terminal phosphorus and a PP multiple bond, respectively, indicating the contribution of resonance structures **3.5'** and **3.5''**. Additionally, the ^{1}H NMR spectrum is symmetrical arguing for a planar geometry, whereas the pyramidalization of the endocyclic phosphorus for **3.7** and **3.12** make those spectra more convoluted. These spectroscopic data support the isolation of free phosphino-phosphinidene **3.5**. In the solid state it can be kept for weeks at room temperature without noticeable decomposition but it is its extremely sensitive to air and moisture. Due to the presence of eight *t*-Bu groups surrounding the molecule, it displayed high solubility in all tested solvents, which prevented the formation of X-ray quality single crystals.



Scheme 3.4: Generation of phosphino-phosphinidene **3.5** by CO elimination from **3.12** and resonance structures **3.5'** and **3.5''**.

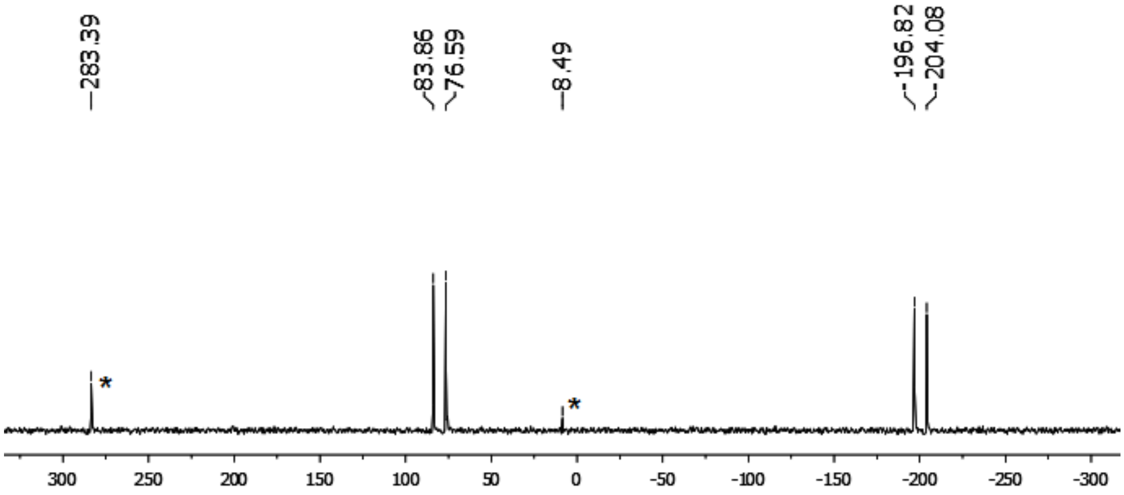
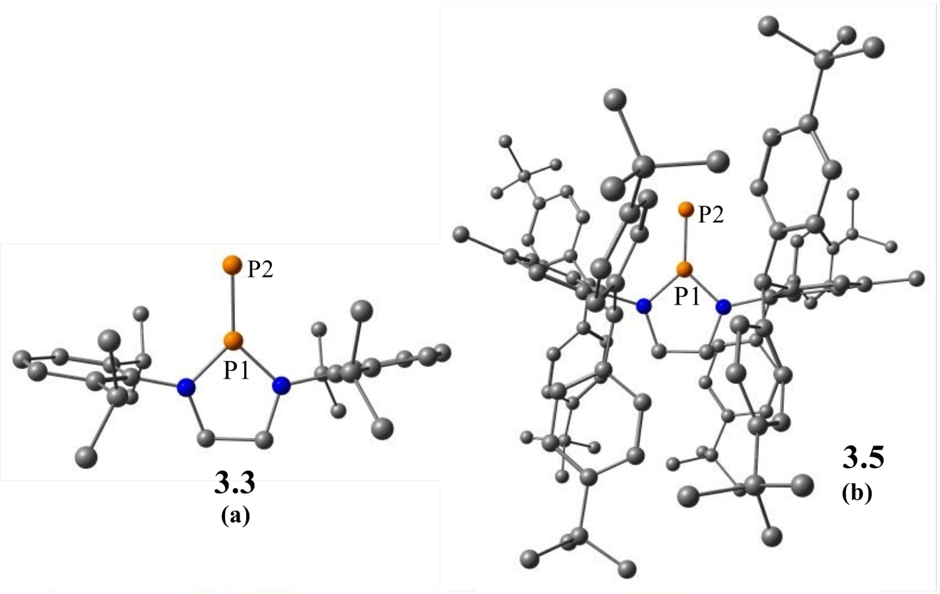


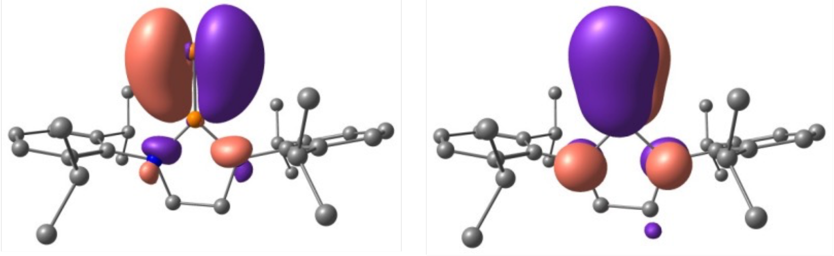
Figure 3.6: ^{31}P NMR spectrum of **3.5**, asterisks denote unidentified impurities.

To gain insight into the electronic structure of phosphino-phosphinidenes, *ab inito* calculations were performed (Figure 3.7). Calculations on **3.5** at the M06-2X/def2-SVP level of theory revealed that the P1-P2 bond length is very short at 1.917 Å, whereas PP double bonds appear around 2.03 Å,[22] and that P1 is indeed in a planar geometry. NBO calculations at the M06-2X/def2-TZVPP//M06-2X/def2-SVP level of theory performed on **3.3** reveal a large WBI for P1-P2 (2.34), which indicates the presence of a PP multiple bond. The HOMO and HOMO-1 also support this, as they are the in-plane and out-of-plane P1-P2 π orbital, respectively, which are polarized toward P2. The HOMO-8 is the P1-P2 σ-bonding orbital, and the LUMO is the P1-P2 π*-antibonding orbital. Natural population analysis shows that P1 carries a large positive charge of +1.16 a.u., while P2 is negatively charged (–0.34 a.u.). From these computational details, the electronic structure that best describes this phosphino-phosphinidene is the zwitterionic form **3.5’**, which is similar as that observed for phosphino-nitrenes.[5]

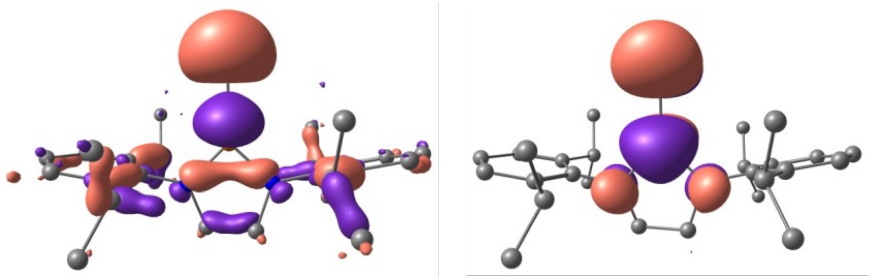


3.3
(a)

3.5
(b)



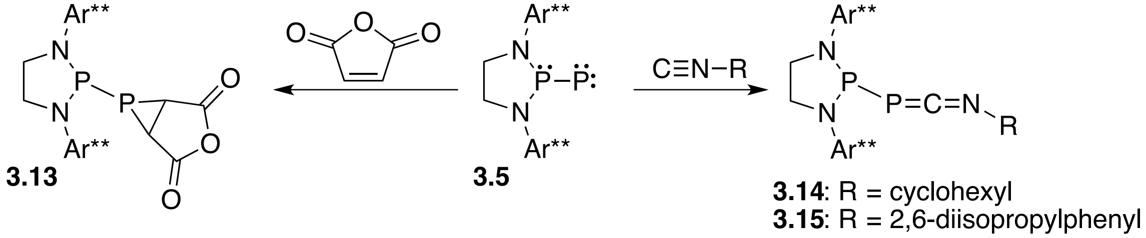
(c) HOMO (-6.56 eV) **(d) HOMO-1 (-6.92 eV)**



(e) HOMO-8 (-10.03 eV) **(f) LUMO (-0.03 eV)**

Figure 3.7: (a and b) Optimized structures of **3.3** and **3.5** showing the protection of the phosphinidene center by 2,6-bis[(4-*tert*-butylphenyl)methyl]-4-methylphenyl substituents (Ar**). The (c) HOMO, (d) HOMO-1, (e) HOMO-8, and (f) LUMO of **3.3**.

In order to experimentally test that this compound mimics the reactivity of nucleophilic carbenes, **3.5** was reacted with an electron-poor alkene. Adding maleic anhydride to **3.5** resulted in full conversion to a new product as observed by ^{31}P NMR spectroscopy after twelve hours. An AX system appearing at 168.5 and –163.0 (J_{PP} = 242.1 Hz) are indicative of phosphirane[29] compound **3.13**.



Scheme 3.5: Reactivity of phosphinidene **3.5** with maleic anhydride and isonitriles, leading to phosphirane **3.13** and phosphacarbodiimides **3.14** and **3.15**.

To further probe the reactivity of **3.5**, we reacted **3.5** with isonitriles. As demonstrated earlier, phosphinidenes undergo [1+1] coupling reactions with these compounds to afford the corresponding phosphacarbodiimides.[26] Mixing **3.5** with cyclohexyl or 2,6-diisopropylphenyl isocyanide resulted in rapid conversion to new products **3.14** and **3.15**, respectively (Scheme 3.5). The ^{31}P NMR spectra of the products showed two doublets (**3.14**: 171.6, –137.0 ppm; **3.15**: 168.9, –158.5 ppm), but with a vastly diminished J_{PP} coupling compared to **3.5** (292 Hz for **3.14**; 305 Hz for **3.15**). Layering hexamethyldisiloxane onto a concentrated benzene solution gave single yellow crystals of **3.15**. The solid-state structure reveals the phosphacarbodiimide and provides a good illustration of the sterically shielding *tert*-butyl substituents of the phenyl groups (Figure 3.8).

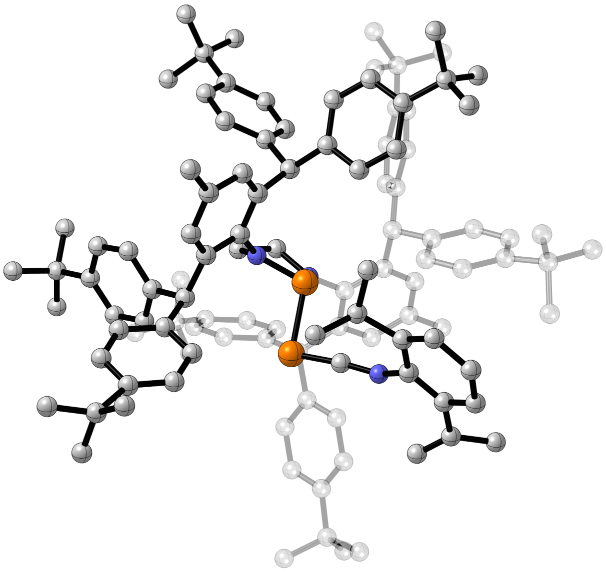


Figure 3.8: Molecular view of **3.15** in the solid state with hydrogen atoms and solvent molecules omitted for clarity.

Conclusion

Singlet phosphinidenes have never been observed as free entities, and we have demonstrated that with the appropriate framework, they can indeed be stable at room temperature. The mesomeric effects of the adjacent phosphorus backbone thermodynamically stabilize the phosphino-phosphinidene, resulting in a high degree of PP multiple bond character. Nevertheless, as expected for a monocoordinated monovalent phosphorus derivative, its reactivity with alkenes and isonitriles is similar to its carbon and nitrogen counterparts. Finally, substantial kinetic protection is crucial to isolate the phosphinidene since they are prone to spontaneously dimerize into the corresponding diphosphene.[30]

Chapter 3 has been submitted for publication. L. Liu, D. A. Ruiz, G. Bertrand, "A Room Temperature Stable Singlet Phosphinidene," *Nature Chem.* The dissertation author was co-primary investigator of this paper.

Appendix: Experimental Section

1) General Information

All manipulations were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under argon and some additionally stored over a potassium mirror (C_6H_6, pentane, and TMS_2O). ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian VX 500 and Bruker 300 at 25 °C. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *sept* = septet, *m* = multiplet, *br* = broad signal. Chemical shifts are given in ppm and coupling constants *J* are given in Hz. Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo-Kα radiation (λ = 0.71073 Å) at the UC San Diego Crystallography Facility. Mass spectra were performed at the UC San Diego Mass Spectrometry Laboratory. Melting points were measured with an electrothermal MEL-TEMP apparatus.

2) General Procedures

Preparation of 3.7: A mixture of **3.6** (1.00 g, 2.25 mmol) and NaPCO•(1,4-dioxane)$_{2.5}$ (0.75 g, 2.90 mmol) was cooled to -78 °C before toluene (20 mL) was added. The mixture was stirred for 15 minutes and then warmed to room temperature. After stirring for 1 hour, the solvent was removed under vacuum and the resulting yellow solid was extracted with 15 mL of pentane. After removing the solvent, **3.7** was obtained as a yellow solid (0.93 g, 88% yield). Yellow single crystals of **3.7** were grown from a saturated pentane solution. M.p.: 130 °C (dec.). ^{1}H NMR (C_6D_6, 300 MHz): δ = 7.13 (m, 6 H), 3.63 (m, 4 H), 3.45 (m, 2 H), 3.16 (m, 2 H), 1.46 (d, *J* = 6.7 Hz, 6 H), 1.28 (d, *J* = 6.7 Hz, 6 H), 1.21 (d, *J* = 7.3 Hz, 6 H) 1.18 (d, *J* = 7.3 Hz, 6H); ^{13}C NMR (C_6D_6, 125 MHz): δ = 194.6 (dd, J_{PC} = 98.2 Hz, J_{PC} = 22.7 Hz), 149.9, 148.2, 135.9, 135.8, 128.5, 124.4, 125.3, 124.7, 124.4, 55.4, 55.3, 29.7, 29.6, 29.3, 29.2, 26.7, 25.6, 25.1, 24.4; ^{31}P NMR (C_6D_6, 121 MHz) δ = 167.7 (d, J_{PP} = 252.1 Hz), -244.5 (d, J_{PP} = 252.1 Hz).

Preparation of 3.8: A solution of **3.7** (35 mg, 0.07 mmol) in 1 mL of pentane was placed in a quartz NMR tube. The mixture was gently heated to obtain a clear solution, which was irradiated for 3 hours. After 1 hour, purple crystals were formed. The solvent was decanted and the crystals were washed with 2 mL of pentane, yielding **3.8** (20 mg, 61% yield) as single purple crystals. M.p.: 210 ºC (dec.). ^{1}H NMR (C_6D_6, 500 MHz): δ = 7.14-7.08 (m, 8H), 6.95 (m, 2H), 6.93 (m, 2H), 3.83 (m, 8H), 3.45 (sept, *J* = 6.6 Hz, 4H), 3.20 (m, 4H), 1.46 (d, *J* = 6.6 Hz, 12H), 1.27 (d, *J* = 6.6 Hz, 12H), 1.07 (d, *J* = 6.6 Hz, 12H), 0.55 (d, *J* = 6.6 Hz, 12H); ^{13}C NMR (C_6D_6, 125 MHz): δ = 149.3, 148.5, 137.7, 127.5, 124.6, 124.3, 55.4, 29.1, 28.8, 25.7, 24.4, 24.0; ^{31}P NMR (C_6D_6, 121 MHz) δ = 675.0 (t, J_{PP} = 75.1 Hz), 137.4 (t, J_{PP} = 75.1 Hz). HRMS: m/z calculated for $[C_{52}H_{77}N_4P_4]^+$ $(M+H)^+$ 881.5093, found 881.5091.

Preparation of 3.9: 30 mg of **3.8** was dissolved in 1 mL of pentane and kept at 40 ºC overnight. The solution was left at room temperature and light yellow crystals grew after a few weeks. The solution was decanted yielding 22 mg of **3.9** (63% yield). M.p.: 180 º C (dec.). ^{1}H NMR (C_6D_6, 500 MHz): δ = 7.13 (br m, 4H), 7.06 (d, *J* = 7.6 Hz, 8H), 3.54 (sept, *J* = 6.8 Hz, 8H), 3.17 (br, 8H), 1.11 (d, *J* = 6.8 Hz, 24H), 1.09 (d, *J* = 6.8 Hz, 24H); ^{13}C NMR (C_6D_6, 125 MHz): δ = 150.2, 138.0, 127.6, 124.7, 52.6, 29.4, 26.7, 24.3; ^{31}P

NMR (C_6D_6, 121 MHz): A_2B_2 spin system, 14 lines resolved $\delta = 63.4$ ($J_{PP} = 360.8$ Hz), 44.5 ($J_{PP} = 360.8$ Hz).

Preparation of 3.10: 1-adamantyl isocyanide (20 mg, 0.12 mmol) and **3.7** (50 mg, 0.11 mmol) were placed in a quartz NMR tube, dissolved in 1.5 mL of cyclohexane and irradiated for 4 hours. The solution was passed through a plug of neutral alumina. The volatiles were removed under vacuum affording **3.10** as a light yellow solid (33 mg, 52% yield). Single crystals were grown from a saturated pentane solution. M.p.: 75 ºC (dec.). ^1H NMR (C_6D_6, 300 MHz): $\delta = 7.16$ (br, 6H), 3.90-3.72 (br m, 6H), 3.31-3.28 (br m, 2H), 1.70 (br, 3H), 1.53 (d, $J = 6.7$ Hz, 6H), 1.50 (br, 3H), 1.43 (d, $J = 6.7$ Hz, 6H), 1.40 (br, 9H), 1.28 (d, $J = 6.5$ Hz, 6H), 1.26 (d, $J = 6.5$ Hz, 6H); ^{13}C NMR (C_6D_6, 125 MHz): $\delta = 185.2$ (dd, $J_{PC} = 80.8$ Hz, $J_{PC} = 30.7$ Hz), 150.3, 148.9, 137.9, 137.8, 128.3, 124.9, 124.3, 55.4, 55.3, 44.1, 36.0, 30.2, 30.0, 29.5, 29.4, 29.2, 29.1, 27.3, 26.0, 25.9, 25.1, 25.0, 24.2; ^{31}P NMR (C_6D_6, 121 MHz): $\delta = 167.5$ (d, $J_{PP} = 272.8$ Hz), –126.9 (d, $J_{PP} = 272.8$ Hz).

Preparation of 3.12: **3.11** (100 mg, 0.07 mmol) and NaPCO•(1,4-dioxane)$_{2.5}$[3] (33 mg, 0.11 mmol) were placed in a Teflon sealed flask. 5 mL of benzene was added and the mixture was stirred for 24 hours. The salts were removed *via* cannula filtration and the volatiles were removed under vacuum, resulting in 86 mg (85% yield) of **3.12** as a yellow solid. M.p.: 285 ºC (dec.). ^1H NMR (C_6D_6, 500 MHz): $\delta = 7.56$ (d, $J = 8.4$ Hz, 4H), 7.37 (d, $J = 8.4$ Hz, 4H), 7.31 (d, $J = 8.4$ Hz, 4H), 7.27 (d, $J = 8.4$ Hz, 4H), 7.25-7.21 (m, 10H), 7.09 (m, 2H), 7.03 (d, $J = 8.4$ Hz, 4H), 6.92 (d, $J = 8.4$ Hz, 4H), 6.85 (s, 1H), 6.84 (s, 1H), 6.46 (s, 1H), 6.45 (s, 1H), 3.02 (br m, 2H), 2.40 (br m, 2H), 1.74 (s, 6H), 1.28 (s, 18H), 1.27 (s, 18H), 1.18 (s, 18H), 1.17 (s, 18H); ^{13}C NMR (C_6D_6, 125 MHz): $\delta = 194.6$

(dd, J_{PC} = 98.0 Hz, J_{PC} = 22.9 Hz), 149.3, 149.0, 148.9, 148.8, 145.7, 144.5, 143.4, 142.1, 141.8, 141.5, 137.1, 136.7, 132.2, 131.7, 131.4, 130.5, 130.3, 129.9, 129.6, 125.8, 125.5, 125.2, 53.9, 53.6, 52.0, 51.2, 34.5, 34.4, 31.7, 31.6, 31.4, 21.1, 21.0; ^{31}P NMR (C_6D_6, 121 MHz): δ = 172.6 (d, J_{PP} = 263.0 Hz), –240.9 (d, J_{PP} = 263.0 Hz).

Preparation of 3.5: **3.12** (80 mg, 0.06 mmol) was placed in a quartz NMR low pressure/vacuum tube and dissolved with 2.5 mL of benzene. The solution was irradiated for 3 hours. Removal of the volatiles afforded **3.5** quantitatively, as a yellow/orange solid. M.p.: 298 ºC (dec.). ^{1}H NMR (C_6D_6, 500 MHz): δ = 7.79 (d, *J* = 8.4 Hz, 8H), 7.31 (d, *J* = 8.4 Hz, 8H), 7.26 (d, *J* = 8.4 Hz, 4H), 7.21-7.19 (m, 12H), 6.81 (s, 4H), 2.61 (s, 4H), 1.74 (s, 6H), 1.27 (s, 36H), 1.19 (s, 36H); ^{13}C NMR (C_6D_6, 125 MHz): δ = 149.1, 149.0, 144.4, 142.9, 141.5, 138.1, 131.1, 130.2, 129.7, 128.6, 125.7, 125.6, 51.5, 34.5, 34.4, 31.6, 31.5, 21.2; ^{31}P NMR (C_6D_6, 121 MHz): δ = 80.2 (d, J_{PP} = 883.7 Hz), –200.4 (d, J_{PP} = 883.7 Hz).

Preparation of 3.13: Maleic anhydride (7 mg, 0.07 mmol) was added to a freshly prepared sample of **3.5** (78 mg, 0.06 mmol) in 2.5 mL of benzene. The mixture was left overnight before the volatiles were removed under vacuum. The residue was extracted with 2 mL of pentane. Removal of the solvent under vacuum afforded 64 mg (77% yield) of **3.13**, as a yellow solid. M.p.: 340 ºC (dec.). ^{1}H NMR (C_6D_6, 500 MHz): δ = 7.34 (d, *J* = 8.4 Hz, 4H), 7.21 (d, *J* = 8.4 Hz, 4H), 7.13-7.10 (m, 17H), 6.95 (m, 3H), 6.88 (d, *J* = 8.4 Hz, 4H), 6.77 (d, *J* = 8.4 Hz, 4H), 6.44 (s, 2H), 6.19 (m, 2H), 2.92 (br m, 2H), 2.48 (d, J_{PH} = 4.5 Hz, 2H), 2.33 (br m, 2H), 1.57 (s, 6H), 1.13 (s, 18H), 1.12 (s, 18H), 1.04 (s, 18H), 1.00 (s, 18H); ^{13}C NMR (C_6D_6, 125 MHz): δ = 168.1, 149.6, 149.5, 149.0, 145.7, 143.4, 142.3, 142.0, 141.5, 141.3, 137.2, 134.5, 132.1, 131.7, 130.4, 130.1, 129.7, 129.6, 126.1, 125.8, 125.6, 125.4, 54.7, 52.6, 51.1, 34.5, 34.4, 34.3, 31.7, 31.6, 31.5, 27.5 (dd, J_{PC} = 46.0 Hz, J_{PC} = 24.9 Hz), 21.0; ^{31}P NMR (C_6D_6, 121 MHz): δ = 168.5 (d, J_{PP} = 242.1 Hz), –163.0 (d, J_{PP} = 242.1 Hz).

Preparation of 3.14: Cylochexyl isocyanide was added to a freshly prepared sample of **3.5** (78 mg, 0.06 mmol) in 2.5 mL of benzene. After, 10 minutes the volatiles were removed under vacuum, the residue was washed with 5 mL of CH_3CN and the remaining solid was dried under vacuum affording 72 mg (86% yield) of **3.14** as a yellow solid. ^{1}H NMR (C_6D_6, 300 MHz): δ = 7.74 (d, *J* = 8.4 Hz, 4H), 7.58 (d, *J* = 8.4 Hz, 4H), 7.35-7.16 (m, 22H), 6.98 (d, *J* = 8.4 Hz, 4H), 6.87 (d, *J* = 8.4 Hz, 4H), 6.66 (s, 1H), 6.64 (s, 1H), 3.37 (br m, 1H), 2.84 (s, 2H), 2.32 (s, 2H), 1.80 (s, 6H), 1.30 (s, 18H), 1.24 (s, 18H), 1.21 (s, 18H), 1.17(s, 18H), 1.25-1.10 (m, 10H); ^{13}C NMR (C_6D_6, 125 MHz): δ = 181.8 (dd, J_{PC} = 82.5 Hz, J_{PC} = 28.9 Hz), 148.9, 148.6, 148.5, 148.4, 146.5, 145.3, 143.9, 143.3, 142.2, 142.1, 138.0, 136.2, 131.4, 131.0, 130.7, 130.5, 129.8, 125.6, 125.4, 125.2, 125.1, 60.0, 53.3, 52.0, 51.4, 50.6, 34.5, 34.4, 32.6, 31.6, 31.5, 25.3, 25.0, 24.5, 22.8, 22.2; ^{31}P NMR (C_6D_6, 121 MHz): δ = 171.6 (d, J_{PP} = 291.6 Hz), –137.0 (d, J_{PP} = 291.6 Hz).

Preparation of 3.15: 2,6-Diisopropylphenyl isocyanide was added to a freshly prepared sample of **3.5** (78 mg, 0.06 mmol) in 2.5 mL of benzene. After, 10 minutes the volatiles were removed under vacuum, the residue was washed with 5 mL of CH_3CN and the remaining solid was dried under vacuum affording 79 mg (90% yield) of **3.15** as a yellow solid. Single yellow crystals were grown by layering hexamethyldisiloxane onto a concentrated benzene solution of **3.15**. M.p.: > 400 ºC.^{1}H NMR (C_6D_6, 300 MHz): δ = 7.75 (d, *J* = 8.4 Hz, 4H), 7.50 (d, *J* = 8.4 Hz, 4H), 7.39 (d, *J* = 8.4 Hz, 4H), 7.28 (d, *J* = 8.4 Hz, 4H), 7.22 (d, *J* = 8.4 Hz, 4H), 7.13-7.05 (m, 7H), 7.02 (d, *J* = 8.4 Hz, 4H), 6.98

(d, J = 8.4 Hz, 4H), 6.81 (d, J = 8.4 Hz, 4H), 6.63 (s, 1H), 6.62 (s, 1H), 3.62 (sept, J = 6.8 Hz, 2H), 2.91 (s, 2H), 2.40 (s, 2H), 1.78 (s, 3H), 1.24 (s, 18H), 1.20 (s, 36H), 1.16 (s, 18H), 1.12 (d, J = 6.8 Hz, 12H); ^{13}C NMR (C_6D_6, 125 MHz): δ = 172.4 (dd, J_{PC} = 87.5 Hz, J_{PC} = 26.7 Hz), 149.0, 148.5, 148.4, 146.6, 145.2, 144.0, 143.4, 142.2, 141.7, 138.1, 136.3, 131.5, 131.2, 130.7, 130.3, 125.5, 125.2, 123.8, 53.5, 52.1, 50.5, 34.4, 31.6, 31.5, 30.0, 23.3, 21.2; ^{31}P NMR (C_6D_6, 121 MHz): δ = 168.9 (d, J_{PP} = 304.6 Hz), –158.5 (d, J_{PP} = 304.6 Hz). HRMS: m/z calculated for $[C_{113}H_{139}N_3P_2Na]^+$ (M+Na)$^+$ 1623.0336, found 1623.0342.

3) Crystallographic Data

Compound	**3.2**
Empirical formula	$C_{27}H_{38}N_2OP_2$
Formula weight	468.53
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	6.3210(7)
b/Å	9.9020(10)
c/Å	21.848(2)
α/°	83.396(3)
β/°	82.860(3)
γ/°	77.508(3)
Volume/Å^3	1319.3(2)
Z	2
ϱ_{calc}g/cm^3	1.179
μ/mm^{-1}	0.186
F(000)	504.0
Crystal size/mm^3	0.25 × 0.20 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.886 to 58.46
Index ranges	$-8 \le h \le 8$, $-13 \le k \le 13$, $-29 \le l \le 29$
Reflections collected	43543
Independent reflections	7163 [R_{int} = 0.0597, R_{sigma} = 0.0360]
Data/restraints/parameters	7163/0/281
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0639, wR_2 = 0.1649

Final R indexes [all data]	$R_1 = 0.0736$, $wR_2 = 0.1734$
Largest diff. peak/hole / e Å^{-3}	1.44/-0.72

Compound	**3.8**
Empirical formula	$C_{52}H_{76}N_4P_4$
Formula weight	881.04
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	9.341(2)
b/Å	12.496(3)
c/Å	12.829(3)
α/°	112.905(6)
β/°	107.678(7)
γ/°	96.822(9)
Volume/Å^3	1265.4(5)
Z	1
ϱ_{calc}g/cm^3	1.156
μ/mm^{-1}	0.187
F(000)	476.0
Crystal size/mm^3	0.22 × 0.18 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.674 to 50.904
Index ranges	$-11 \le h \le 11$, $-15 \le k \le 15$, $-15 \le l \le 15$
Reflections collected	18459
Independent reflections	4645 [$R_{int} = 0.1518$, $R_{sigma} = 0.1345$]
Data/restraints/parameters	4645/237/279
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	$R_1 = 0.0573$, $wR_2 = 0.1249$
Final R indexes [all data]	$R_1 = 0.1093$, $wR_2 = 0.1505$
Largest diff. peak/hole / e Å^{-3}	0.35/-0.50

Compound	**3.9**
Empirical formula	$C_{28.5}N_2P_2$
Formula weight	432.24
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	13.4249(2)
b/Å	20.2092(4)
c/Å	10.4936(2)
α/°	90.00

β/°	90.00
γ/°	90.00
Volume/Å^3	2846.98(9)
Z	4
ρ_{calc}g/cm^3	1.008
μ/mm^{-1}	1.499
F(000)	860.0
Crystal size/mm^3	0.25 × 0.2 × 0.18
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.9 to 124.86
Index ranges	$-15 \leq h \leq 15$, $-20 \leq k \leq 23$, $-12 \leq l \leq 12$
Reflections collected	20872
Independent reflections	4522 [R_{int} = 0.0538, R_{sigma} = 0.0428]
Data/restraints/parameters	4522/0/295
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0609, wR_2 = 0.1817
Final R indexes [all data]	R_1 = 0.0632, wR_2 = 0.1858
Largest diff. peak/hole / e Å^{-3}	0.56/-0.33
Flack parameter	0.02(3)

Compound	**3.10**
Empirical formula	$C_{37}H_{53}N_3P_2$
Formula weight	601.76
Temperature/K	100(2)
Space group	P-1
a/Å	9.9108(9)
b/Å	12.4616(12)
c/Å	15.6415(15)
α/°	102.139(3)
β/°	91.150(3)
γ/°	111.398(3)
Volume/Å^3	1748.4(3)
Z	2
ρ_{calc}g/cm^3	1.143
μ/mm^{-1}	0.153
F(000)	652.0
Crystal size/mm^3	0.14 × 0.11 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.68 to 50
Index ranges	$-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-18 \leq l \leq 18$
Reflections collected	45928
Independent reflections	6154 [R_{int} = 0.0501, R_{sigma} = N/A]
Data/restraints/parameters	6154/93/399

Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	$R_1 = 0.0774$, $wR_2 = 0.1906$
Final R indexes [all data]	$R_1 = 0.0970$, $wR_2 = 0.2072$
Largest diff. peak/hole / e Å^{-3}	1.01/-0.69

Compound	**3.15**
Empirical formula	$C_{119}H_{145}N_3P_2$
Formula weight	1679.31
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	15.3624(15)
b/Å	16.9295(17)
c/Å	22.503(2)
α/°	93.727(3)
β/°	101.498(3)
γ/°	113.657(3)
Volume/Å^3	5184.3(9)
Z	2
ρ_{calc}g/cm^3	1.074
μ/mm^{-1}	0.090
F(000)	1815.0
Crystal size/mm^3	0.02 × 0.02 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.986 to 50
Index ranges	$-18 \leq h \leq 18$, $-20 \leq k \leq 20$, $-25 \leq l \leq 27$
Reflections collected	103705
Independent reflections	18262 [$R_{int} = 0.0422$, $R_{sigma} = 0.0332$]
Data/restraints/parameters	18262/170/1381
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	$R_1 = 0.0777$, $wR_2 = 0.2067$
Final R indexes [all data]	$R_1 = 0.1160$, $wR_2 = 0.2505$
Largest diff. peak/hole / e Å^{-3}	0.43/-0.41

4) Computational Details

Calculations were carried out with the Gaussian 09 package.[31] Geometry optimizations were performed with the M06-2Xfunctional.[32] The def2-SVP[33,34] basis set was used for all the atoms. Frequency calculations at the same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum) and provide frontier molecular orbitals (HOMOs and LUMOs). To reduce the computational cost, the 2,6-diisopropylphenyl groups were used for the natural bond orbital (NBO) calculations at the M06-2X/def2-TZVPP//M06-2X/def2-SVP level of theory. The Cartesian coordinates and the sum of electronic and zero-point energies are as follows:

3.1 (singlet)

ΔE (ZPE) = -871.436505 a.u.

15	0.519714	0.000005	-0.000010
15	2.424645	-0.000001	0.000010
7	-0.665666	1.188277	0.162706
7	-0.665663	-1.188276	-0.162741
6	-2.005745	0.745043	-0.180149
1	-2.220664	0.873546	-1.256441
1	-2.767989	1.289610	0.394496
6	-2.005731	-0.745052	0.180174
1	-2.220603	-0.873556	1.256476
1	-2.767997	-1.289625	-0.394437
1	-0.399978	-2.155530	-0.018888
1	-0.399999	2.155541	0.018891

3.1 (triplet)

ΔE (ZPE) = -871.408709 a.u.

15	0.414346	-0.378767	0.889924
15	1.986018	0.164946	-0.609233
7	-0.651863	-1.259422	-0.142437
7	-0.646379	0.989082	0.841927
6	-1.726348	-0.431323	-0.697815
1	-2.678376	-0.635264	-0.180671
1	-1.871800	-0.617641	-1.773224
6	-1.318815	1.025046	-0.449548
1	-0.654278	1.372652	-1.265518
1	-2.199461	1.682796	-0.419031
1	-0.275751	1.876697	1.170153
1	-0.967117	-2.141881	0.245673

3.2 (singlet)

ΔE (ZPE) = -1332.847596 a.u.

15	-0.000033	0.597676	-0.000414
15	-0.000188	2.507101	-0.000432
7	-1.217494	-0.585866	0.018288
6	3.476785	-1.119912	-0.747171
6	-3.138158	0.729470	-0.770267
6	-2.609239	-0.316673	-0.005538
7	1.217556	-0.585789	-0.019296
6	2.609270	-0.316537	0.005376
6	3.137743	0.729663	0.770327
6	4.510861	0.967793	0.769689
1	4.908383	1.789868	1.366835
6	5.372805	0.161027	0.030175
1	6.447205	0.348059	0.040100
6	-4.511267	0.967592	-0.768813
1	-4.909202	1.789599	-1.365778
6	-5.372751	0.160862	-0.028702
1	-6.447160	0.347884	-0.038016
6	-3.476264	-1.119993	0.747614
6	-0.723381	-1.933543	-0.239346
1	-0.784973	-2.162652	-1.318261
1	-1.314938	-2.681637	0.303482
6	0.723488	-1.933523	0.238283
1	0.785122	-2.162667	1.317189
1	1.315058	-2.681557	-0.304604
6	4.848504	-0.887209	-0.725734
1	5.509759	-1.522083	-1.317574
6	-4.848008	-0.887308	0.726980
1	-5.508903	-1.522150	1.319258
1	2.469719	1.359429	1.356517
1	3.070477	-1.920795	-1.366721
1	-2.470451	1.359185	-1.356879
1	-3.069531	-1.920812	1.366973

3.2 (triplet)

ΔE (ZPE) = -1332.834503 a.u.

15	-0.000316	-0.688531	-0.253807
15	-0.213362	-1.439967	1.855343
7	1.248521	0.493586	-0.023513
6	-2.999580	-0.786375	-1.110910
6	3.055289	-1.123465	-0.193159
6	2.602589	0.209974	-0.158784
7	-1.181796	0.587032	-0.255804
6	-2.549753	0.281838	-0.312418
6	-3.496912	1.024136	0.408696
6	-4.853621	0.712129	0.318069
1	-5.572250	1.305610	0.885872
6	-5.293114	-0.344775	-0.472293
1	-6.354429	-0.586003	-0.534895
6	4.407948	-1.408883	-0.335099
1	4.729516	-2.451474	-0.360890
6	5.349241	-0.383527	-0.429758
1	6.409993	-0.611499	-0.534589

6	3.555922	1.239846	-0.249767
6	0.769543	1.851420	0.185840
1	0.915481	2.455472	-0.727415
1	1.316292	2.338264	1.009146
6	-0.714551	1.727277	0.514501
1	-0.862044	1.566987	1.601629
1	-1.263921	2.633704	0.223066
6	-4.352108	-1.092659	-1.183336
1	-4.675346	-1.923854	-1.812250
6	4.909304	0.936911	-0.381739
1	5.628978	1.754434	-0.453208
1	2.342248	-1.945228	-0.095409
1	3.241875	2.282870	-0.229134
1	-3.182550	1.847103	1.049277
1	-2.276928	-1.366318	-1.688075

3.3 (singlet)
ΔE (ZPE) = -1803.692545 a.u.

15	-0.011014	-0.233133	0.616462
15	0.004004	-0.348157	2.523967
7	1.188772	-0.100844	-0.560457
6	-3.533680	-0.989756	-0.325962
6	3.133109	-3.561057	-0.984436
1	3.047929	-3.124037	-1.990341
1	2.588419	-4.516665	-0.974069
1	4.196619	-3.778889	-0.802856
6	2.575985	-2.614794	0.084486
1	1.509175	-2.458285	-0.134085
6	3.270763	-1.264776	0.033839
6	2.586318	-0.076479	-0.275153
7	-1.231111	-0.222587	-0.556542
6	-2.595974	0.059007	-0.238291
6	-2.980077	1.366446	0.114343
6	-4.330767	1.602232	0.394045
1	-4.651178	2.607428	0.676730
6	-5.267859	0.579613	0.315740
1	-6.317094	0.783982	0.535336
6	2.665904	-3.233816	1.481799
1	2.109126	-4.181917	1.516752
1	2.241933	-2.552141	2.232231
1	3.711512	-3.446454	1.753048
6	4.643572	-1.184589	0.295651
1	5.195377	-2.093873	0.544190
6	5.312660	0.031439	0.242376
1	6.383421	0.073469	0.448325
6	3.250345	1.167049	-0.338003
6	0.713578	-0.336181	-1.917302
1	0.816019	-1.403607	-2.190631
1	1.300745	0.257828	-2.633184
6	-0.754275	0.088704	-1.899610
1	-0.853103	1.172272	-2.102377
1	-1.346754	-0.454486	-2.651073
6	-4.871555	-0.706142	-0.045209
1	-5.617083	-1.499647	-0.107521
6	-1.993614	2.521386	0.197042
1	-0.989170	2.146771	-0.054720
6	-2.332715	3.615571	-0.820761
1	-2.372209	3.214950	-1.844649
1	-1.577797	4.415466	-0.789047
1	-3.311280	4.069917	-0.602963
6	-1.920270	3.086991	1.618122
1	-2.888396	3.513034	1.923436
1	-1.167136	3.887055	1.675112
1	-1.646737	2.298802	2.333685
6	-3.077348	-2.399165	-0.661414
1	-2.206302	-2.308138	-1.328347
6	-4.139360	-3.225483	-1.385246
1	-4.982155	-3.470544	-0.721557
1	-3.707588	-4.178606	-1.722961
1	-4.538642	-2.697159	-2.263248
6	-2.606687	-3.113882	0.611601
1	-1.816122	-2.547264	1.124034
1	-2.223453	-4.117907	0.373939
1	-3.446408	-3.223813	1.315090
6	3.293674	3.481989	-1.397523
1	4.092897	3.906031	-0.771504
1	2.647787	4.317232	-1.704512
1	3.756555	3.053422	-2.298261
6	4.620728	1.198372	-0.076101
1	5.159389	2.145979	-0.117371
6	2.475812	2.441178	-0.633411
1	1.616319	2.162407	-1.263162
6	1.917663	3.037874	0.665329
1	1.307488	2.309578	1.219949
1	1.299846	3.923677	0.449295
1	2.743992	3.347101	1.324138

3.3 (triplet)
ΔE (ZPE) = -1803.665108 a.u.

15	-0.049319	-0.245931	-0.856884

15	0.183514	-2.405341	-1.475371
7	1.172708	-0.144818	0.366106
6	-2.931536	1.463409	0.345460
6	2.329160	3.756904	0.345424
1	2.418927	3.479762	1.405727
1	1.562445	4.541753	0.256007
1	3.287993	4.194068	0.027625
6	1.954833	2.545669	-0.514308
1	0.971530	2.192985	-0.173629
6	2.942828	1.405608	-0.333270
6	2.541162	0.120401	0.095911
7	-1.250202	-0.317912	0.360334
6	-2.604972	0.095840	0.213591
6	-3.607323	-0.863721	-0.036771
6	-4.931899	-0.436419	-0.164769
1	-5.716038	-1.170023	-0.364381
6	-5.262364	0.909704	-0.051473
1	-6.300134	1.229397	-0.158842
6	1.828469	2.930979	-1.991222
1	1.099658	3.744748	-2.120912
1	1.496394	2.072309	-2.592615
1	2.795489	3.275202	-2.390177
6	4.296339	1.633596	-0.598962
1	4.614276	2.621932	-0.938995
6	5.243878	0.631424	-0.424015
1	6.297143	0.830738	-0.628123
6	3.497435	-0.907527	0.267333
6	0.687028	-0.272099	1.734956
1	0.670487	0.717857	2.230748
1	1.335345	-0.933953	2.331886
6	-0.728855	-0.844661	1.615062
1	-0.690288	-1.952827	1.604096
1	-1.373713	-0.531438	2.448443
6	-4.267055	1.848874	0.199979
1	-4.533772	2.904180	0.288191
6	-3.267951	-2.331123	-0.226054
1	-2.217190	-2.468773	0.066337
6	-4.117822	-3.248158	0.655923
1	-4.036953	-2.968392	1.716256
1	-3.789047	-4.292136	0.547990
1	-5.181360	-3.206694	0.375730
6	-3.387516	-2.714222	-1.704875
1	-4.430181	-2.622213	-2.047115
1	-3.058486	-3.751867	-1.867260
1	-2.766843	-2.057858	-2.333662
6	-1.865636	2.512911	0.605334
1	-0.952932	1.979600	0.909974
6	-2.244419	3.468430	1.738601
1	-3.101012	4.102794	1.464722
1	-1.401241	4.137024	1.967417
1	-2.508423	2.919651	2.654094
6	-1.549760	3.282570	-0.682076
1	-1.201474	2.601561	-1.473152
1	-0.766411	4.035701	-0.503720
1	-2.447432	3.804361	-1.049156
6	3.687655	-2.628303	2.099115
1	4.788094	-2.634623	2.069647
1	3.354561	-3.620453	2.438580
1	3.382394	-1.884418	2.849616
6	4.842517	-0.626576	0.012287
1	5.588279	-1.413602	0.145957
6	3.109452	-2.307096	0.716568
1	2.012042	-2.345034	0.784511
6	3.537492	-3.362325	-0.307738
1	3.140606	-3.129661	-1.306580
1	3.165885	-4.355652	-0.014256
1	4.634071	-3.422345	-0.382299

3.4 (singlet)

ΔE (ZPE) = -3413.961007 a.u.

15	0.256302	0.162960	-0.735944
15	0.237819	0.121623	-2.646542
7	0.718794	-0.947347	0.447694
6	-0.248958	3.692813	0.079286
6	3.467649	-1.654898	0.038430
1	3.019316	-0.676931	-0.203898
6	2.356372	-2.683319	-0.090039
6	1.023056	-2.302595	0.143061
7	-0.228612	1.280989	0.440156
6	-0.941242	2.466401	0.097513
6	-2.303873	2.407885	-0.236073
6	-2.948781	3.584389	-0.631352
1	-4.004472	3.536905	-0.911176
6	-2.281405	4.807995	-0.669713
6	2.638295	-4.011939	-0.407981
1	3.674620	-4.301245	-0.599873
6	1.626335	-4.970171	-0.500602
6	-0.017118	-3.247483	0.040421
6	0.855825	-0.354352	1.775137
1	1.873293	0.049579	1.928463

1	0.671938	-1.113874	2.548764
6	-0.184754	0.767906	1.808919
1	-1.172753	0.386060	2.122578
1	0.107037	1.567455	2.507229
6	-0.932270	4.847460	-0.295824
1	-0.401337	5.802706	-0.302037
6	-3.087572	1.112823	-0.075865
1	-2.392365	0.275441	-0.252045
6	1.234582	3.705898	0.436825
1	1.354412	3.038256	1.304029
6	0.309019	-4.567261	-0.273183
1	-0.494211	-5.304448	-0.352131
6	-1.476488	-2.855617	0.244881
1	-1.467411	-1.819063	0.619361
6	-3.606139	0.949502	1.349134
6	-3.928221	2.035949	2.167913
6	-3.779845	-0.342183	1.861537
6	-4.413072	1.832796	3.461853
1	-3.791215	3.053317	1.797959
6	-4.256395	-0.550170	3.153353
1	-3.529755	-1.198977	1.233351
6	-4.577411	0.542349	3.960448
1	-4.658830	2.694310	4.085207
1	-4.368679	-1.570426	3.525943
1	-4.951577	0.387996	4.973700
6	-4.172321	0.947721	-1.135382
6	-5.530564	0.853493	-0.826132
6	-3.773766	0.864743	-2.476176
6	-6.476714	0.684920	-1.840972
1	-5.857562	0.906435	0.213858
6	-4.716147	0.699526	-3.485458
1	-2.707879	0.922796	-2.717851
6	-6.074209	0.608209	-3.171202
1	-7.535297	0.614528	-1.584482
1	-4.387348	0.630767	-4.524001
1	-6.814700	0.477131	-3.962156
6	-2.292737	-2.835445	-1.049706
6	-3.690323	-2.713879	-0.990700
6	-1.684824	-2.852380	-2.307888
6	-4.453248	-2.597909	-2.149058
1	-4.197585	-2.726755	-0.023776
6	-2.448943	-2.744005	-3.471750
1	-0.599552	-2.926343	-2.386402
6	-3.832479	-2.614167	-3.397914
1	-5.536130	-2.483310	-2.073963
1	-1.947911	-2.751682	-4.441249
1	-4.427909	-2.518912	-4.307515
6	-2.102688	-3.693445	1.352041
6	-2.758931	-4.902757	1.095165
6	-1.986096	-3.267217	2.679262
6	-3.273066	-5.668892	2.140060
1	-2.885674	-5.237341	0.063028
6	-2.501105	-4.029049	3.727154
1	-1.492336	-2.314141	2.890440
6	-3.145782	-5.235843	3.459559
1	-3.783974	-6.607890	1.920828
1	-2.402568	-3.674696	4.754779
1	-3.553464	-5.834361	4.275533
6	3.997650	-1.535249	1.462719
6	3.701851	-2.459889	2.466766
6	4.803591	-0.433432	1.786544
6	4.192421	-2.284147	3.763958
1	3.075234	-3.324135	2.239039
6	5.291280	-0.254683	3.077077
1	5.055235	0.289134	1.005818
6	4.983850	-1.182488	4.074787
1	3.950086	-3.017535	4.534919
1	5.913293	0.611849	3.307504
1	5.363681	-1.045656	5.088344
6	4.558526	-1.872995	-1.001399
6	5.829222	-2.356471	-0.684371
6	4.252452	-1.592434	-2.340656
6	6.781314	-2.555882	-1.687924
1	6.081263	-2.574748	0.355457
6	5.201715	-1.788113	-3.339142
1	3.254600	-1.214507	-2.587882
6	6.472037	-2.270992	-3.014859
1	7.771057	-2.933316	-1.425360
1	4.950420	-1.562541	-4.377232
1	7.217989	-2.422481	-3.796658
6	1.715973	5.078963	0.890341
6	1.261399	5.571080	2.121962
6	2.578772	5.873212	0.132144
6	1.652310	6.824394	2.581392
1	0.583347	4.958603	2.722718
6	2.971599	7.133254	0.590606
1	2.955195	5.504517	-0.823202
6	2.511420	7.613161	1.813183
1	1.288782	7.188020	3.544068
1	3.646991	7.739515	-0.015362

1	2.822721	8.595848	2.170722
6	2.079285	3.102560	-0.673443
6	3.148540	2.258193	-0.352038
6	1.820259	3.377641	-2.017940
6	3.940122	1.698865	-1.353797
1	3.357576	2.037301	0.699813
6	2.613654	2.822860	-3.021919
1	0.969511	4.009410	-2.283114
6	3.672249	1.978588	-2.693814
1	4.767393	1.031880	-1.099817
1	2.388045	3.035792	-4.068138
1	4.284754	1.526336	-3.475684
6	1.934126	-6.399379	-0.862407
1	1.466723	-7.095547	-0.151545
1	1.543335	-6.639519	-1.862593
1	3.015591	-6.585436	-0.868572
6	-2.983156	6.068305	-1.102929
1	-2.859947	6.864046	-0.354143
1	-2.564070	6.442480	-2.049119
1	-4.056653	5.896852	-1.253072

3.4 (triplet)
ΔE (ZPE) = -3413.923614 a.u.

15	0.105303	-0.333889	-1.095639
15	0.922792	-2.286220	-1.895537
7	1.321696	-0.039136	0.127773
6	-3.152501	0.422891	0.362086
6	1.194421	2.808366	-0.645743
1	0.359909	2.158426	-0.339618
6	2.485526	2.105290	-0.269883
6	2.516135	0.714765	-0.047068
7	-1.015365	-0.787446	0.126315
6	-2.437525	-0.740467	0.022970
6	-3.151815	-1.898575	-0.379739
6	-4.541442	-1.872927	-0.422469
1	-5.081232	-2.767724	-0.741013
6	-5.265929	-0.729565	-0.063056
6	3.679862	2.827353	-0.279794
1	3.636934	3.908068	-0.442772
6	4.917189	2.203738	-0.117062
6	3.763708	0.060724	0.068197
6	0.814244	-0.178037	1.492389
1	0.481176	0.807246	1.875748
1	1.592042	-0.555111	2.170890
6	-0.351407	-1.147174	1.382189
1	0.027710	-2.185632	1.362721
1	-1.063630	-1.059410	2.215671
6	-4.553514	0.398278	0.322683
1	-5.101698	1.305212	0.586903
6	-2.388973	-3.172723	-0.713590
1	-1.504979	-2.863874	-1.289900
6	-2.472924	1.733279	0.748078
1	-1.387348	1.547804	0.746225
6	4.938634	0.813794	0.026759
1	5.899392	0.297064	0.096594
6	3.811051	-1.454681	0.217270
1	2.940705	-1.834738	-0.334315
6	0.990282	4.099303	0.137056
6	1.103223	5.372516	-0.425003
6	0.663393	3.995009	1.495637
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6	-6.770953	-0.738256	-0.103366
1	-7.177245	-1.472579	0.608013
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3.5 (singlet)

ΔE (RM062X) = -4671.51340441 a.u.

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7	-0.019527	1.032170	-0.855867
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Conclusion

We have demonstrated that several reactive species could be stabilized with the proper supporting framework. Since our report of the first neutral, nucleophilic, tricoordinate boron derivative, compounds of these types have attracted increasing interest. A new approach was developed to synthesize these compounds, which allows for fine-tuning by the supporting carbenes. The isolation of different unsymmetrically substituted derivatives of type $(L_1)(L_2)BH$ was illustrated (Figure C.1). The electronic properties of the carbenes around the boron center played a role in the stabilization of the molecule. The more π-accepting CAAC ligand proved to serve a pivotal role, while the less electrophilic carbenes acted similar to spectator ligands. An innovative synthesis was also developed to generate a carbene-stabilized boryl anion, where the traditional polarity of the boron-hydrogen bond was inverted, allowing for deprotonation at the BH moiety. This research has given insights into strategies to further develop the emerging field of stable nucleophilic boron chemistry.

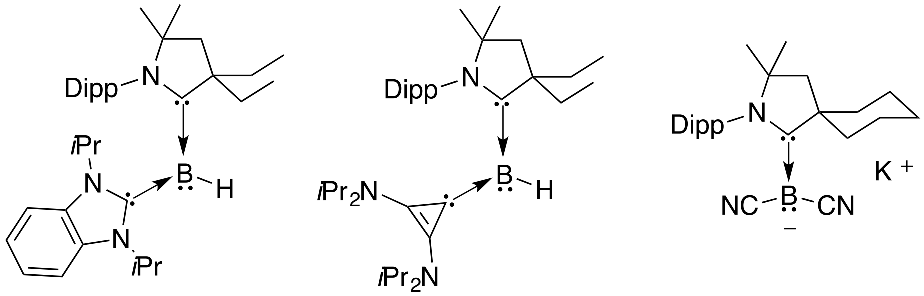

Figure C.1: Boron centered nucleophiles.

The steric environment of carbenes is a factor to consider when attempting to isolate highly reactive species. We demonstrated that the previously unknown parent phosphenium fragment and its derivatives can be structurally elucidated and stored for months, thanks to the stabilization of a bulky NHC (Figure C.2). If a smaller NHC is used, the parent phosphenium cannot be isolated, demonstrating that the steric bulk protects the fragment from decomposition.

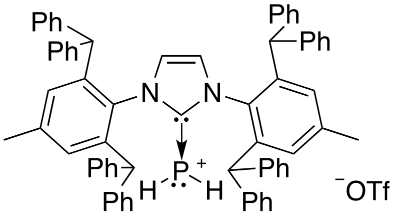

Figure C.2: The parent phosphenium ion stabilized by a bulky NHC.

The contrast between classical NHCs and CAACs has become increasingly apparent. The peculiar electronic properties of CAACs have given it an advantage in isolating a broad range of low valent compounds compared to NHCs. We demonstrated that to be the case as well with antimony. An NHC was reported to be ineffective at stabilizing low valent antimony adducts, but we showed that a CAAC could stabilize antimony in four different oxidation states (Figure C.3). This demonstrates the non-innocent nature of the CAAC ligand and is a rare example of a single ligand stabilizing an element in several oxidation states.

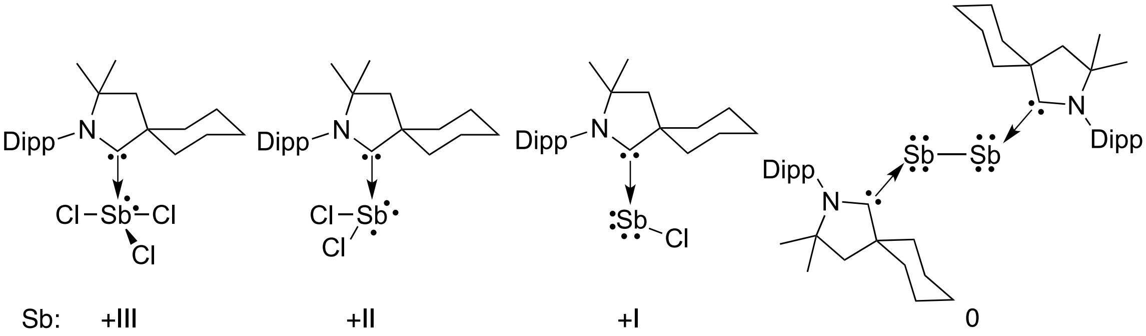

Figure C.3: Four different oxidation states of anatomy stabilized by a CAAC.

More than two decades after the isolation of a stable carbene and numerous efforts towards stable phosphinidenes, this long-standing target has been achieved. We demonstrated that with the appropriate framework a phosphino-phosphinidene was capable of being tamed under ambient conditions. The mesomeric effects of the backbone along with the extremely sterically shielding substituents provide both electronic stabilization and kinetic protection. Without the bulky substituents, the phosphinidene will dimerize into the corresponding diphosphene (Figure C.4).

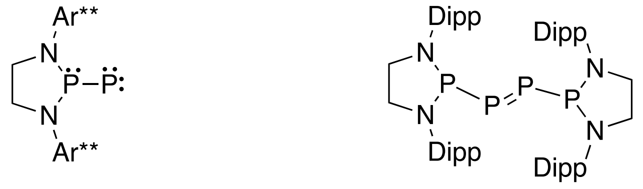

Figure C.4: The first stable phosphinidene and a diphosphene resulting from phosphinidene dimerization; Ar** = 2,6-bis[(4-*tert*-butylphenyl)methyl]-4-methylphenyl.

Overall, the stabilization of these molecules gives additional insights for the stabilization of hitherto unknown fragments. Although the notion of using carbenes, which once were considered highly reactive species, to stabilize highly reactive species sounds nonsensical, we demonstrated that they are in fact powerful stabilizing entities. With the initial isolation of a stable phosphinidene, future applications similar to carbenes could potentially be found as well as some unexpected ones.